

Hund's rule in metal clusters: Prediction of high magnetic moment state of Al_{12}Cu from first-principles calculations

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Using *ab initio* pseudopotential plane wave method and generalized gradient approximation for the exchange and correlation energy, we report the finding of high spin ground state of Al_{12}Cu cluster in accordance with the Hund's rule of maximum spin at half-filling. It has perfect icosahedral symmetry and a magnetic moment of $3\mu_B$, forming an *open shell* superatom. Further studies of its interaction with an Al atom have led to an electronically closed shell magic cluster with 1.68 eV highest occupied–lowest unoccupied molecular orbital (HOMO-LUMO) gap such that the added Al atom is incorporated within the cage around the Cu atom.

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The ground states of atoms are known to follow Hund's rule of maximum spin. However, aggregates of atoms have reduced spin due to delocalization of electrons and spatial Jahn-Teller distortions that are often energetically more favorable than atomlike high symmetry and high spin states. Some clusters of *s-p* bonded metals show atomlike behavior and are also referred to as superatoms.¹ In most cases these have closed electronic shells and zero spin similar to rare gas atoms and in general, the ground state is of lowest spin. High-spin solutions have been obtained from spherical jellium model (SJM) calculations² and for certain high symmetric structures³ that have not been found to be the ground states from atomic calculations. Atomlike behavior and Hund's rule have, however, been observed in quantum dots.⁴ Here, we report the finding of a large magnetic moment of $3\mu_B$ in an Al_{12}Cu cluster in accordance with Hund's first rule, making it an *open shell superatom*. Its interaction with an Al atom further leads to a new magic cluster, Al_{13}Cu .

Clusters of alloys are interesting for novel nanomaterials as their atomic distributions and compositions could be quite different from bulk. Aluminum alloys are technologically important due to their light weight, and many of these have clusters as their building blocks.⁵ Studies of the electronic structure and bonding in clusters provide a fundamental understanding of phenomena at the nanoscale and could give useful insight into the properties of complex alloys from a local point of view.⁶

We use an *ab initio* ultrasoft pseudopotential method^{7,8} with a plane wave basis. The exchange-correlation energy is calculated within the generalized gradient approximation⁹ with spin polarization. A simple cubic supercell of size 15 Å is used with only the Γ point for Brillouin zone integrations. The cutoff energy for the plane wave expansion is taken to be 17.18 Ry. The converged structures are further optimized with a cutoff of 21.47 Ry and the results remain nearly unchanged. The method of Methfessel and Paxton¹⁰ is used to smear the states for achieving self-consistency. Structural relaxations are performed on a few selected isomers without any symmetry constraint using the conjugate gradient method. This search, though it samples a limited phase space, is believed to have led to the true ground state of this

cluster. The converged structures are reoptimized using the Gaussian method with a 6-311+G* basis and Perdew-Wang 1991 (PW91) exchange correlation,¹¹ and the results reaffirm the conclusions obtained from the pseudopotential method.

Table I summarizes the results of the structure, binding energy (BE), magnetic moments, and the gap for the studied clusters. Al_{12}Cu has odd number of electrons but surprisingly the lowest-energy structure is found to be a regular icosahedron with Cu at the center. The center to vertex and vertex to vertex bond lengths are 2.64 and 2.77 Å, respectively. This is nearly an ideal closest packing with 13 atoms. Its electronic spectrum (Fig. 1) can be described within the SJM of *sp* bonded metals excluding the *3d* states of Cu. The latter hybridize with the other states⁶ of the cluster, but are quite localized on the Cu ion. In SJM, electronic levels *1s*, *1p*, *1d*, *2s*, *1f*, *2p*, . . . are progressively filled with 2, 8, 18, 20, 34, 40, . . . valence electrons as the cluster size increases. Thus, excluding the 10 *3d* electrons of Cu, there are 37 valence electrons, which is 3 more than the *1f* shell closing at 34. These 3 electrons are accommodated in the spin-up *2p* jellium states, leaving the spin-down *2p* states completely empty with a net magnetic moment of $3\mu_B$ on this cluster. This is in accordance with Hund's rule of maximum spin at half-filling. When calculations are done forcing a doublet state (ions relaxed), the energy is found to lie 0.088 eV higher, confirming the higher-spin state to be the ground state. To our knowledge, this is the first result in the size

TABLE I. Structure, BE per atom, magnetic moments (M) and HOMO-LUMO gap of studied clusters. (G) refers to Gaussian calculations. (1) and (2) refer to isomers where the impurity atom is at the center and outside of the Al_{13} cluster, respectively.

Cluster	Structure	BE (eV)	$M(\mu_B)$	Gap (eV)
Al_{12}Cu	I_h	2.595	3.0	0.414
	I_h (G)	2.520	3.0	0.488
Al_{13}Cu	C_{3v} (1)	2.728	0.0	1.684
Al_{13}Cu	C_{3v} (2)	2.695	0.0	1.705
Al_{13}Ag	C_{3v} (1)	2.585	0.0	1.438
Al_{13}Ag	C_{3v} (2)	2.645	0.0	1.778

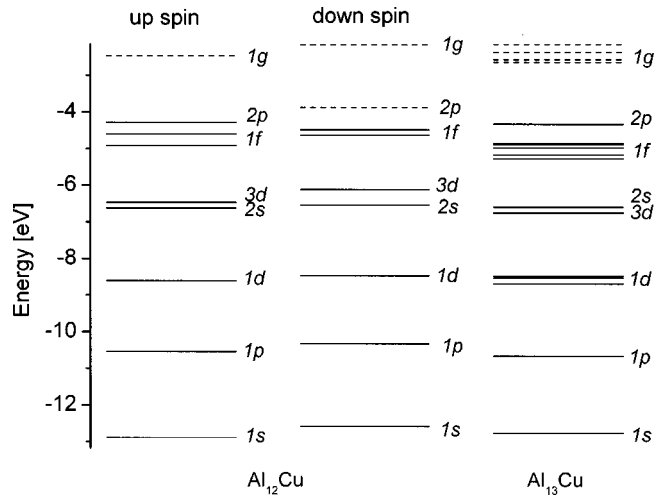


FIG. 1. Ground state electronic spectra of Al_{12}Cu (spin-polarized) and Al_{13}Cu clusters with Cu at the center of the Al_{12} and Al_{13} shells, respectively. The occupied (unoccupied) states are shown by solid (dashed) lines and labeled according to the spherical jellium model leaving aside the $3d$ states of Cu.

range of 13 atoms in which a cluster favors a high magnetic moment state as compared to a low-spin state with Jahn-Teller distortions. This is important in the study of superatoms as it shows that clusters with higher magnetic moments can be created from its constituents, here the Cu atom and Al_{12} cluster, which themselves have lower net magnetic moments. Aluminum clusters in this size range have either a 0 or 1 μ_B magnetic moment¹ depending upon even or odd number of atoms, respectively.

In order to understand the origin of this large magnetic moment, we carried out a spin-polarized calculation on icosahedral Al_{12} shell. It has a net magnetic moment of $2\mu_B$ with the spin-up $2p$ states partly occupied. Addition of a Cu atom at the center leads to the full occupation of the spin-up states. The exchange splitting for the $2p$ states is 0.414 eV and the embedding energy of Cu in the Al_{12} shell is 4.271 eV. This is quite large as compared to the BE of Al_{12}Cu (2.595 eV/atom). The latter is nearly the same as for Al_{13} (Ref. 12), which is also a slightly distorted icosahedron. Substitution of small size Cu in place of Al at the center of Al_{13} , however, improves the bonding and packing between aluminum atoms on the shell that are strained in Al_{13} . This reduction in strain can favor icosahedral growth even for larger clusters. This could be significant to understand the role of Cu in the stabilization of aluminum-based quasicrystals.

Further optimizations of a decahedron and a cuboctahedron with Cu at the center show the cuboctahedron to relax to the icosahedral isomer. The magnetic moment remains the same ($3\mu_B$) during this transformation, and therefore it is likely to be robust. The decahedral isomer favors Jahn-Teller distortions [Fig. 2(a)] with a magnetic moment of 1 μ_B and lies 0.08 eV higher in energy. Also substitution of Cu at the vertex of an icosahedron is 0.872 eV higher in energy than at the center. It also has a magnetic moment of $3\mu_B$ despite the reduced symmetry. This gives us confidence that a high-spin state is the true ground state of this cluster. The bulk BE's of

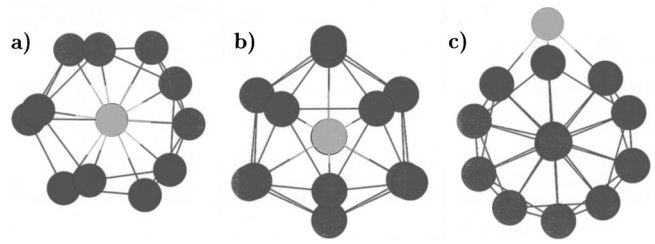


FIG. 2. Atomic structures of (a) relaxed decahedral Al_{12}Cu , (b) Al_{13}Cu with Cu at the center, and (c) Al_{13}Cu with Cu outside the Al_{13} cluster. Similar structures are obtained for Al_{13}Ag . For Al_{13}Cu (b) has lower energy but for Al_{13}Ag , (c) is lower in energy.

Al and Cu are nearly equal (3.39 and 3.49 eV/atom, respectively). Therefore, a large difference in the BE's for Cu at the center and the vertex further reflects the importance of the icosahedral structure with the smaller atom at the center. Calculations with the Gaussian method give the high-spin ground state to be 0.146 eV lower in energy than the doublet state, in close agreement with the above results (Table I).

The total and the spin-up $2p$ density isosurfaces (Figs. 3(A)–3(C)) show delocalization of charge over the whole cluster with the highest density around the Cu ion. The spin-up density is more on the top of the aluminum and around the Cu ions. There is some covalent character in the Al-Al bonds [Fig. 3(A)], which have high density as compared to the centers of the faces. This is remarkably similar to the charge distribution in the Al_{12} shell, which also shows some covalent character [Fig. 3(D)]. The difference between the charge density of Al_{12}Cu and the superposition of the charge densities of the Al_{12} shell and the Cu atom at the respective positions of Al_{12}Cu shows significant excess around the copper ion [Fig. 3(E)] and a small excess outside the Al shell (not seen in the figure as the density is low). This is in agreement with the Pauling electronegativities of Cu (1.9) and Al (1.5). There is a slight depletion of charge in the Al-Al bonds [Fig. 3(F)] and very close to the Cu ion. Therefore, *the covalent character in the Al_{12} shell is slightly weakened by the presence of Cu at the center* and a strong bonding is developed between the Cu and Al_{12} shell. Covalent character was found to develop¹³ in Al-Al bonds in the case of Al-Li clusters due to charge transfer from Li to Al ions. Therefore, the direction of charge transfer seems to be important in determining the strength of covalent bonding between the aluminum ions. These results on clusters are relevant for bulk alloys as charge transfers are predominantly local and are likely to be similar as it is indeed found¹³ in the case of Al-Li. Note that covalent bonding in Al-Al bonds has recently been found in Al-Mn-Si quasicrystals.¹⁴ The bonding nature in these systems could be an important factor to understand the brittle and semiconductorlike behaviors of some quasicrystal-forming alloys.

The electronic structure of Al_{12}Cu suggests that this *open shell superatom* could have properties similar to atoms with a half-filled p level. The unoccupied spin-down states of Al_{12}Cu may accept three electrons to complete the shell. We, therefore, studied its interaction with an Al atom at a three-fold site. Structural relaxation leads to incorporation of the added Al atom within the cage [Fig. 2(b)]. It has C_{3v} sym-

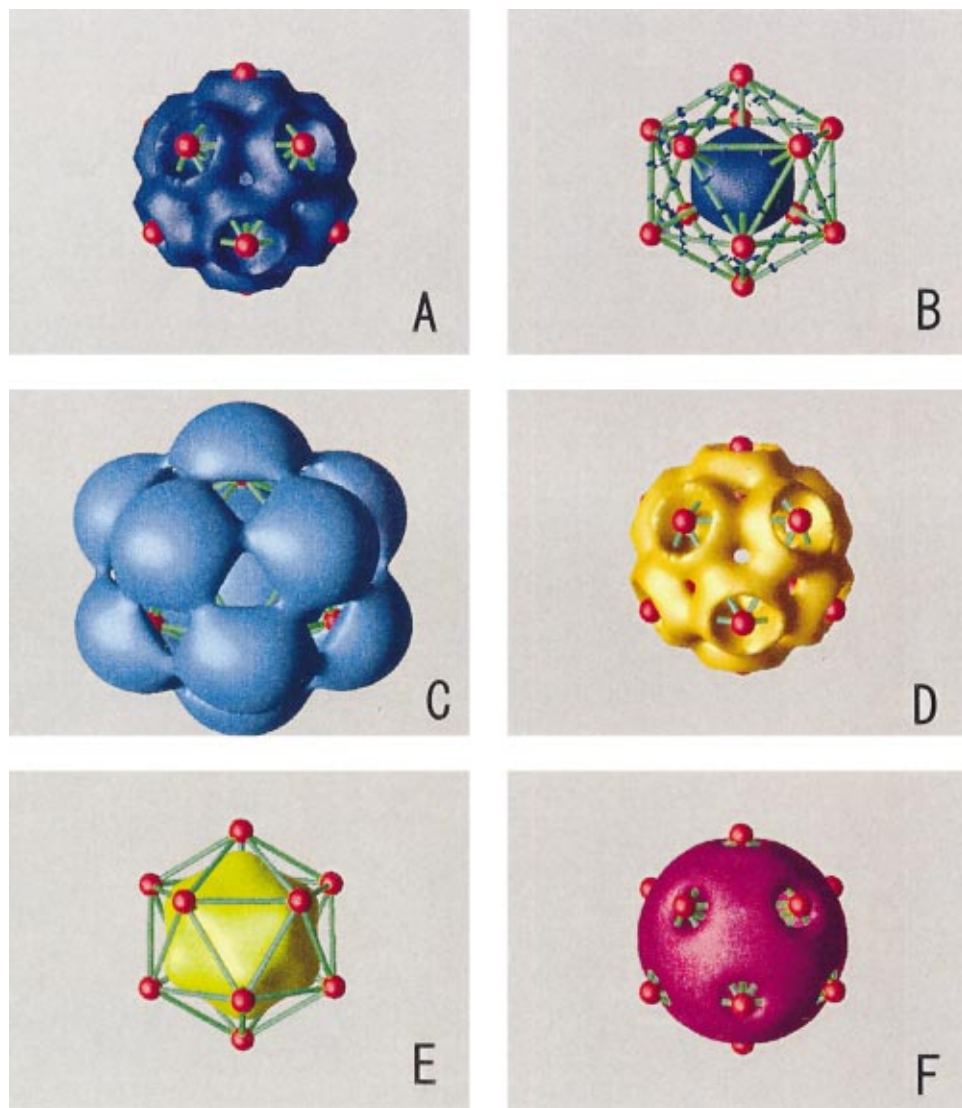


FIG. 3. (Color) Electronic charge density isosurfaces for Al_{12}Cu . Red balls represent the Al ions. (A) and (B) show the total charge density isosurfaces at (A) $0.207 e/\text{\AA}^3$ and (B) $0.237 e/\text{\AA}^3$. (C) shows the isosurface for spin-up charge density at $0.0089 e/\text{\AA}^3$ and (D), the isosurface of total charge density in Al_{12} , at $0.207 e/\text{\AA}^3$. Note the similarity with the isosurface in (A). (E) and (F) show, respectively, the isurfaces of the excess ($0.003 e/\text{\AA}^3$) and depletion ($0.006 e/\text{\AA}^3$) of charge as compared to the overlapping charge densities of Al_{12} and Cu at the respective positions in Al_{12}Cu .

metry but there are large variations in the bond lengths with Cu closely bonded to 10 Al ions [2.43 (3), 2.52 (1), 2.64 (3) and 2.77 (3) Å] and loosely to 3 Al ions (3.01 Å). The nearest neighbor Al-Al bond lengths are in the range of 2.55–3.11 Å. Therefore, *Cu ion in Al_{13}Cu is similar to a caged ion in an endohedral fullerene and is likely to be quite mobile*. The BE of Al on Al_{12}Cu is 4.45 eV, which is again quite high as compared to the BE of Al_{12}Cu . The highest occupied molecular orbital–lowest unoccupied molecular orbital, HOMO-LUMO, gap is 1.684 eV and it should make Al_{13}Cu a very stable magic cluster similar to the 40-valence-electron clusters^{1,12,15} of the *sp* bonded metals. As expected, the unoccupied spin-down *2p* states of Al_{12}Cu are now occupied (Fig. 1).

As Al_{13} is itself a near magic cluster; another interesting possibility for Al_{13}Cu is one in which a Cu atom interacts with Al_{13} . Structural relaxations show it to be stable at the threefold site [Fig. 2(c)] but 0.463 eV higher in energy as compared to the isomer with Cu at the center. The bond lengths in this case also have a large spread (2.40 Å between Cu and three neighboring Al ions, which themselves are far apart at 3.22 Å) due to charge transfer from Cu to

Al_{13} . This makes the latter a closed shell cluster with a large HOMO-LUMO gap of 1.705 eV. The BE of Cu on Al_{13} is 3.872 eV. Substitution of Ag in place of Cu is, however, favorable outside Al_{13} by 0.848 eV than at the center. This is due to the bigger size of Ag atom that also results in a lower BE of 3.211 eV. The HOMO-LUMO gap is large (1.778 eV) and should make this cluster abundant similar to alkali-metal (Li or Na) doped^{13,15} Al_{13} .

The electronic charge density in Al_{13}Cu (Fig. 4) also shows some covalent character in a few Al-Al bonds [Figs. 4(A) and 4(B)] that have short lengths (2.55, 2.61, 2.64, and 2.71 Å). There are low-density parts (some other bonds [Fig. 4(A)] and the centers of triangular faces [Fig. 4(B)]). The difference in the charge density of Al_{13}Cu and the overlapping densities of Al_{13} shell and Cu at the respective positions [Figs. 4(C)–4(F)] shows excess charge between the Cu and a few Al ions [three above and one below in Fig. 4(E)]. However, it is not so significant as compared to Al_{12}Cu due to different behaviors of Al_{12} and Al_{13} cages. Rather, there is a spill-out of charge [Fig. 4(E)]. Therefore, the charge transfer and covalent character depend upon the environment of aluminum ions around the Cu ion.

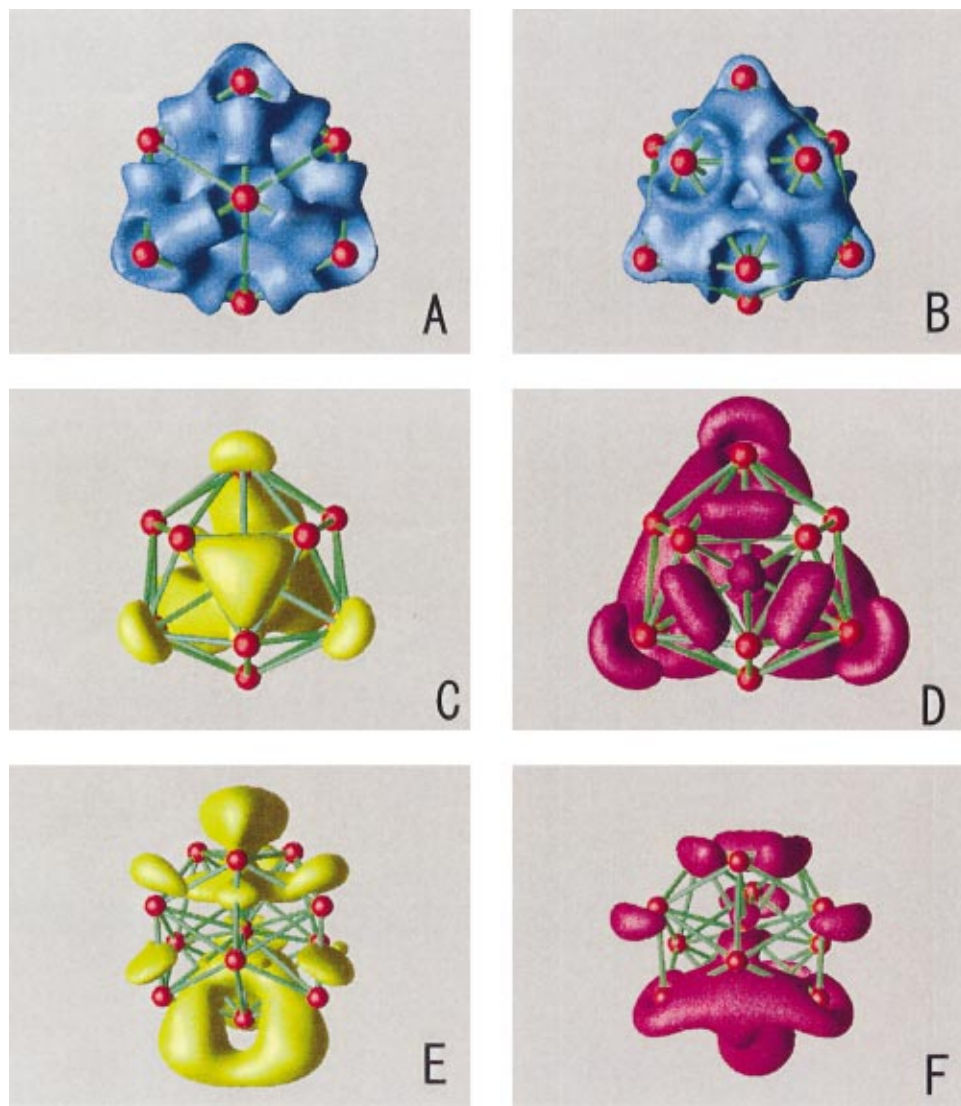


FIG. 4. (Color) Same as in Fig. 3 but for Al_{13}Cu . (A) and (B) show the total charge density isosurfaces at 0.207 (one side) and 0.228 $e/\text{\AA}^3$ (opposite side), respectively. Note the high density in some bonds. (C) and (D) show the excess and depletion of charge as compared to the overlapping charge densities of Al_{13} and Cu atom at the values of 0.0089 $e/\text{\AA}^3$. (E) and (F) show the side view corresponding to (C) and (D), respectively.

In summary, we find Al_{12}Cu cluster to have a high-spin lowest-energy state in accordance with Hund's rule of maximum spin at half-filling. Similar to atoms with half-filled p states, it forms an open shell superatom and should be abundant, in particular, in a triply charged configuration. Its interaction with an Al atom further leads to a new magic cluster, Al_{13}Cu , with a large BE and 1.684 eV HOMO-LUMO gap. We hope that these results would stimulate experiments to look for the new magic clusters and high magnetic moments in Al_{12}Cu as well as in other clusters. Also, the improved geometric packing, bonding nature, and the existence of a large gap near the HOMO in Al_{12}Cu could have significant bearing on the understanding of the stability and other properties of aluminum-based quasicrystals.

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Note added in proof: In a recent paper,¹⁶ the abundance spectrum of Al_nCu anions show large abundance for $n = 13$ in agreement with our prediction. The structure of Al_{12}Cu is reported to be a distorted icosahedron in contrast to our result of a perfect icosahedron with high magnetic moment. Also the structure of Al_{13}Cu differs from the one we have obtained.

¹V. Kumar, K. Esfarjani, and Y. Kawazoe, in *Clusters and Nanomaterials*, edited by Y. Kawazoe, T. Kondow, and K. Ohno, Vol. XXX of Springer Series in Cluster Physics (Springer-Verlag,

Heidelberg, 2001), p. 9.

²A. Hintermann and M. Manninen, *Phys. Rev. B* **27**, 7262 (1983); C. Kohl, B. Montag, and P.-G. Reinhard, *Z. Phys. D: At., Mol.*

- Clusters **35**, 57 (1995).
- ³I.I. Geguzin, JETP Lett. **33**, 568 (1981).
- ⁴S. Tarucha *et al.*, Phys. Rev. Lett. **77**, 3613 (1996); M. Bayer *et al.*, Nature (London) **405**, 923 (2000).
- ⁵W.B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys* (Wiley, New York, 1982).
- ⁶X.G. Gong and V. Kumar, Phys. Rev. B **50**, 17 701 (1994); in *Proceedings of the 5th International Conference on Quasicrystals*, edited by C. Janot and R. Mosseri (World Scientific, Singapore, 1995), p. 484.
- ⁷G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996); Comput. Mater. Sci. **6**, 15 (1996).
- ⁸D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
- ⁹J.P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991).
- ¹⁰M. Methfessel and A.T. Paxton, Phys. Rev. B **40**, 3616 (1989).
- ¹¹M.J. Frisch *et al.*, GAUSSIAN 98, Revision A.9 (Gaussian, Inc., Pittsburgh PA, 1998).
- ¹²V. Kumar, S. Bhattacharjee, and Y. Kawazoe, Phys. Rev. B **61**, 8541 (2000).
- ¹³V. Kumar, Phys. Rev. B **60**, 2916 (1999).
- ¹⁴K. Kiriwara *et al.*, Phys. Rev. Lett. **85**, 3468 (2000).
- ¹⁵V. Kumar, Phys. Rev. B **57**, 8827 (1998).
- ¹⁶S. N. Khanna, C. Ashman, B. K. Rao, and P. Jena, J. Chem. Phys. **114**, 9792 (2001).