Collectivization of Electronic Spin Distributions and Magneto-Electronic Properties of Atomic Clusters of Ga and In with As, V, and Mn

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Exponential increase in nano- and sub-nanoscale research has involved investigations of the microscopic nature and origin of magnetism, including a search for the smallest atomic clusters that possess collectivized electronic spin density distributions. In this work the Hartree-Fock (HF) and restricted open-shell HF (ROHF) methods have been used to synthesize virtually (i.e., fundamental theory-based, computationally) a set of small pyramidal clusters of Ga or In atoms with As, V, and Mn atoms. The majority of the clusters are not destabilized by inclusion of vanadium or manganese atoms. The cluster charge and spin density distributions are collectivized. The In-based clusters with V or Mn atoms possess relatively large spin density values that may be of interest for spintronic materials development.

Index Terms—**Bonding, charge carrier density, magnetooptic effects, quantum dots.**

I. INTRODUCTION

RECENT advances in experimental techniques to manipulate a single electron spin in a quantum dot [1] or a position of a "magnetic" atom in a semiconductor crystal [2] fueled an interest to magnetic quantum dots, artificial molecules and atomic clusters as a mean to realize simultaneously advantages of semiconductor-based nanotechnologies [3] and molecular magnetism, in a quest for the development of new classes of devices, such as chips and ICs with integrated logic and storage, exciton lasers and sensors, etc. These experimental studies have been followed by theoretical investigations [4] of electronic and magnetic properties of atomic clusters that provide insight into their structure, composition, and magneto-electronic properties.

In the work reported here a virtual (i.e., fundamental theory-based, computational) synthesis method [5] is applied to the development of several stable atomic clusters composed of a few semiconductor compound atoms (Ga, In and As) and one or two vanadium or manganese atoms. Pre-designed $Ga_{10}As_4$ and $In_{10}As_4$ clusters virtually synthesized in [5] from pyramidal symmetry elements of the zincblende lattices of GaAs and InAs have been used as a starting point. The pyramidal frames of these clusters are built of 10 Ga or In atoms with four As atoms placed at $1/4$ of the cube body diagonals in the original lattices (and thus inside of the pyramidal frames of the Ga or In atoms). The covalent radii of Ga, In and As atoms in these original clusters are 1.26 Å, 1.44 Å, and 1.18 Å, respectively (known from experiment).

In the Ga- and In-based clusters so obtained, one or two As atoms have been replaced by one or two vanadium or manganese atoms, without any changes to the positions of the remaining Ga or In and As atoms. [These spatial constraints have been incorporated to reflect effects of quantum confinement on artificial molecules synthesized in such a confinement.] The HF/ROHF

methods (as realized by the GAMESS software package [6]) have been further applied to study these clusters, leading to the development of pre-designed artificial molecules $Ga_{10}As_3V$, $Ga_{10}As_2V_2$, $In_{10}As_3V$, $In_{10}As_2V_2$, and $In_{10}As_3Mn$. Thus, the Schrödinger equation in each case has been solved to obtain the ground state of the corresponding clusters (or rather, artificial molecules) in the presence of the boundary conditions corresponding to the spatial constraints applied to the atomic positions. The corresponding "vacuum" clusters (relaxed versions of the pre-designed ones) have been developed by relaxing the spatial constraints applied to the atomic positions in the pre-designed clusters and subsequent optimization (solving the corresponding Schrödinger equations in the absence of the spatial constraints).

II. MAGNETO-ELECTRONIC PROPERTIES OF THE CLUSTERS

A. Structure and Charge Density Distributions

Electronic configurations of the atoms used in this work are collected in Table I. The artificial molecules virtually synthesized of these atoms by the HF/ROHF energy minimization procedure possess all of the features of molecules, including the well-defined ground states (Table II), electronic energy level structures, and highly collectivized electronic charge and spin densities depicted in Figs. 1–5. Both Ga-based molecules with one vanadium atom each are ROHF triplets. The vacuum molecule remains almost pyramidal in shape [Fig. 1(a)]. The vacuum cluster $Ga_{10}As_2V_2$ with two vanadium atoms appears to be unstable, while the corresponding pre-designed cluster has been stabilized. This result indicates that quantum confinement may have a major impact on the outcome of molecular synthesis, in particular allowing synthesis of non-stoichiometric molecules that may not exist otherwise. The CDDs of all of the pre-designed clusters reach beyond the space occupied by cluster atoms, and further than the CDDs of the corresponding vacuum clusters. This means that the "surfaces" of the pre-designed clusters are more charged than those of their vacuum counterparts. In-based vacuum clusters with V atoms deviate slightly more from the pyramidal shape than the Ga-based vacuum cluster. In all cases, the CDD values are somewhat larger in the vicinity of V atoms and neighboring Ga or In

TABLE I
GROUND STATES OF THE USED SEMICONDUCTOR COMPOUND ATOMS

Atom	Electronic Configuration	Atomic Term	Nuclear Spin	Nuclear Magnetic Moment, in Units of μ_P
^{31}Ga	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p$	$^2P_{1/2}$	3/2	2.0166
^{49}In	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p$	$^2P_{1/2}$	9/2	5.5340
^{33}As	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$	$^4S_{3/2}$	3/2	1.4395
^{23}V	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$	$^4F_{3/2}$	7/2	5.1574
^{25}Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$	$^6S_{5/2}$	5/2	3.4687

$\mu_P = e\hbar/2m_P$, where e is the electron charge, $\hbar = h/2\pi$ and m_P is the proton mass.

TABLE II
RHF-ROHF GROUND STATE DATA FOR THE STUDIED CLUSTERS

| Clusters	Spin Multiplicity, M, and Ground State Energy, $(-1) \times 1$ Hartree	Direct Optical Transition Energy, eV
$Ga_{10}As_3V$	M=3; 2660.42732327	1.2626
$Ga_{10}As_3V$ (VC)	M=3; 2660.50877876	1.0585
$Ga_{10}As_2V_2$	M=7; 2724.87162702	0.8735
$Ga_{10}As_2V_2$ (VC)	Not stable	
$In_{10}As_3V$	M=9; 1971.48038779	0.0571
$In_{10}As_3V$ (VC)	M=5; 1971.42527523	1.2653
$In_{10}As_2V_2$	M=11; 2035.9308104	0.1551
$In_{10}As_2V_2$ (VC)	M=1; 2035.72470138	3.6082
$In_{10}As_3Mn$	M=1; 2003.69191872	3.9076
$In_{10}As_3Mn$ (VC)	M=7; 2004.23909571	1.2436

Abbreviation VC denotes vacuum clusters.
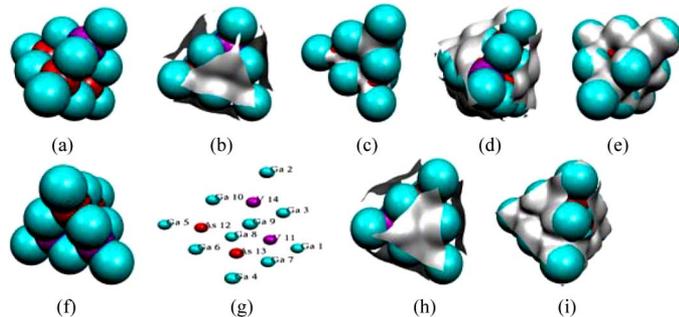
Fig. 1. Structure and charge density distributions (CDDs) of gallium-based clusters. (a) The structure of the vacuum $Ga_{10}As_3V$ cluster; (b) to (e): the CDDs of the pre-designed [(b) and (c)] and vacuum (d) and (e) $Ga_{10}As_3V$ clusters; gray surfaces correspond to fractions (cuts) 0.01 [(b) and (d)], 0.04 (c) and 0.03 (e) of the CDD maximum values (10.3218 and 10.4387, respectively, in arbitrary units; not shown). The structure (f), atomic positions (g) and CDD [gray surfaces, (h) and (i)] of the pre-designed $Ga_{10}As_2V_2$ cluster; cuts 0.01 (h) and 0.02 (i) refer to the CDD maximum value 10.2974 in arbitrary units (not shown). Vanadium atoms are violet, gallium blue, As red. All dimensions, but in (g), are to scale.

atoms, signifying that V atoms accumulate electronic charge (Fig. 2). In contrast, the presence of a Mn atom in $In_{10}As_3Mn$ clusters leads to a significant charge accumulation on the "surfaces" of the clusters in the vicinity of the In atoms surrounding the corresponding Mn atoms (Fig. 3), rather than in the regions surrounding the Mn atoms themselves, which are relatively charge-poor. This result correlates with experimental evaluations [2] of the role of Mn atoms in GaAs bulk lattices, where Mn atoms are believed to donate holes. The ground state energy
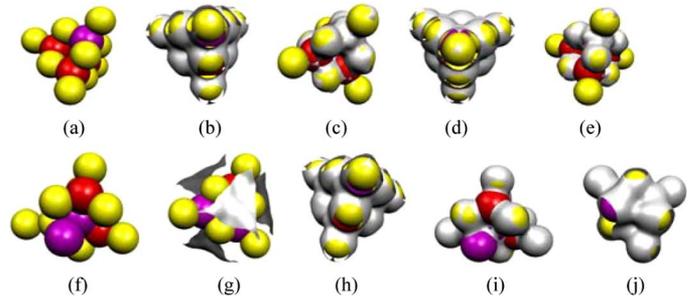

Fig. 2. Structure and charge density distributions (CDDs) of indium-based clusters with vanadium atoms. (a) The structure of the vacuum $In_{10}As_3V$ cluster; (b) to (e): the CDD of the pre-designed [(b) and (c)] and vacuum (d) and (e) $In_{10}As_3V$ clusters; gray surfaces correspond to fractions (cuts) 0.05 [(b) and (d)] and 0.08 [(c) and (e)] of the CDD maximum values (3.54328 and 3.49717, respectively, in arbitrary units; not shown). The structure (f) of the vacuum $In_{10}As_2V_2$ cluster; the CDDs [gray surfaces, (g) to (j)] of the pre-designed [(g) and (h)] and vacuum [(i) and (j)] $In_{10}As_2V_2$ clusters; cuts 0.01 [(g) and (i)], 0.05 (h) and 0.005 (j) refer to the CDD maximum values (3.44417 and 3.01461, respectively, in arbitrary units; not shown). Vanadium atoms are the darkest (violet), indium the lightest (yellow), As red. All dimensions are approximately to scale.
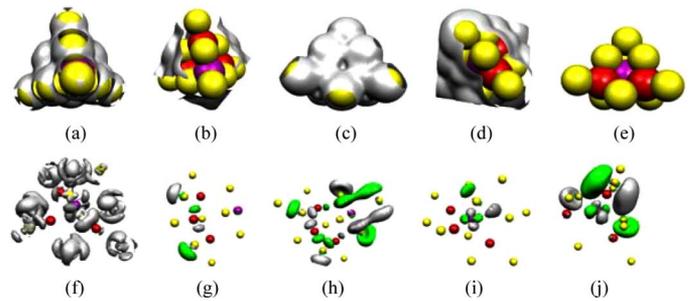

Fig. 3. CDDs of the pre-designed [(a) and (b)] and vacuum [(c) and (d)] $In_{10}As_3Mn$ clusters; gray surfaces correspond to the fractions (cuts) 0.05 [(a) and (c)] and 0.001 [(b) and (d)] of the CDD maximum values (4.25145 and 4.61805, respectively, in arbitrary units; not shown). The structure (e) and SDD (f) of the vacuum $In_{10}As_3Mn$ cluster; cut 0.005 refers to the SDD maximum values 0.045847 in arbitrary units; not shown). The HOMOs of the pre-designed [(g) and (h)] and vacuum [(i) and (j)] $In_{10}As_3Mn$ clusters; cuts 0.05 [(g) and (i)] and 0.03 [(h) and (j)] refer to the maximum and minimum values (not shown; darker and lighter surfaces, respectively) of the HOMOs. Manganese atoms are the darkest (violet), indium the lightest (yellow), As red. Atomic dimensions in (f) to (j) are reduced.

of the $In_{10}As_3Mn$ molecules is significantly lower than that of the respective $In_{10}As_3$ V molecules (Table II). This indicates that Mn atoms may be included more easily into zincblende lattices than V atoms, again in agreement with experiment. In all studied cases quantum confinement has a significant effect on the direct optical transition energy (OTE, Table II). Although the displacement of atoms in vacuum molecules from their respective positions in the pre-designed molecules is small (in the range of several tenths of Angstrom, at most), the ground states and the OTEs of the vacuum molecules may differ from those of their pre-designed counterparts up to an order of magnitude.

B. Spin Density Distributions and Bonding

Understandably, the more excited is the ground state of a molecule, the larger are values of its SDD (Figs. 3 to 5). Similar
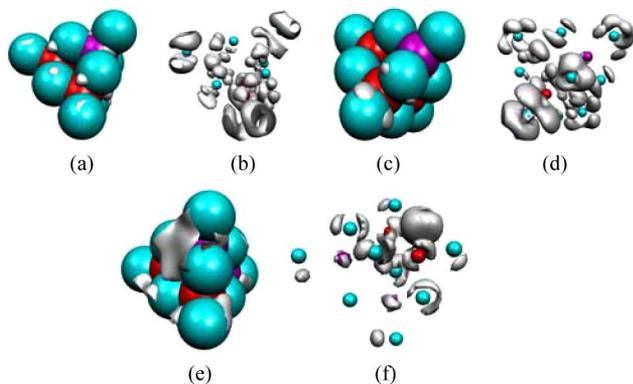
Fig. 4. Spin density distributions (SDDs) of the pre-designed [(a) and (b)] and vacuum [(c) and (d)] $Ga_{10}As_3V$ cluster; gray surfaces correspond to the fractions (cuts) 0.001 of the SDD maximum values (0.0164589 and 0.0354054, respectively, in arbitrary units; not shown). The SDD [(e) and (f)] of the pre-designed $Ga_{10}As_2V_2$ cluster, cuts 0.001 (e) and 0.005 (f) refer to the SDD maximum value 0.0234998, in arbitrary units (not shown). Vanadium atoms are the darkest (violet), gallium the lightest (blue), As red. Atomic dimensions are reduced in (b), (d) and (f).
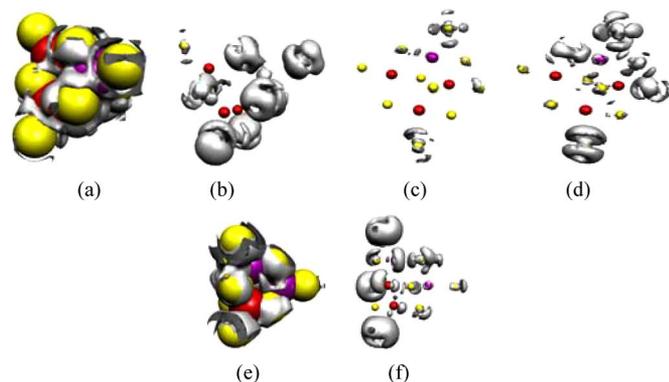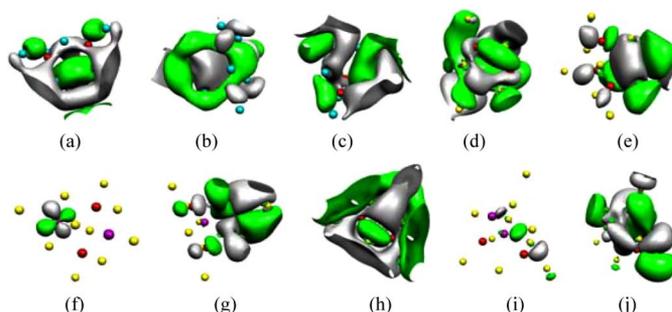

Fig. 6. HOMOs of the clusters with vanadium atoms. Surfaces of both signs [positive (darker) and negative (lighter)] correspond to the fractions (cuts) of the HOMO maximum and minimum values (not shown), respectively. Pre-designed (a) and vacuum (b) $Ga_{10}As_3V$ clusters, cuts 0.005. The pre-designed $Ga_{10}As_2V_2$ cluster (c), cut 0.005. Pre-designed (d) and vacuum (e) $In_{10}As_3V$ clusters, cuts 0.008. Pre-designed [(f) to (h)] and vacuum [(i) and (j)] $In_{10}As_2V_2$ clusters, cuts 0.05 [(f) and (i)], 0.005 (g), 0.008 [(h) and (j); the LUMO surfaces are depicted in (h)]. Vanadium atoms are violet, indium yellow, As red. Atomic dimensions are reduced.

Fig. 5. Spin density distributions (SDDs) of indium-based clusters with vanadium atoms. The pre-designed [(a) and (b)] and vacuum [(c) and (d)] $In_{10}As_3V$ clusters; gray surfaces correspond to the fractions (cuts) 0.001 (a), 0.005 [(b) and (d)], and 0.01 (c) of the SDD maximum values (0.0773016 and 0.046256, respectively, in arbitrary units; not shown). The pre-designed $In_{10}As_2V_2$ cluster; cuts 0.001 (e) and 0.005 (f) refer to the SDD maximum value 0.0893445 (in arbitrary units; not shown). Vanadium atoms are violet, indium yellow, As red. Atomic dimensions in (b), (c), (d) and (f) are reduced. The SDD of the vacuum $In_{10}As_2V_2$ cluster is zero.

to the CDDs, the SDDs of all of the studied clusters are collectivized and spread over the cluster space, slightly accumulating around Ga or In atoms, rather than V or Mn atoms. The major contributions to the SDDs come from electrons in 3d atomic orbitals (AOs) of Ga or In atoms. The pre-designed $In_{10}As_2V_2$ molecule possesses the largest values of the SDD, while the SDD values of the Ga-based molecules are the smallest. Vanadium and manganese atoms subtly choreograph the SDDs, rather than define the major contributions to them. These indirect effects are further demonstrated by the nature of bonding in the studied molecules (Fig. 6), which are non-stoichiometric

and do not obey the octet rule [5], [7]. In particular, for a given molecule, up to 100 electrons participate in the bonding contributing to a set of higher occupied molecular orbitals (MOs). The nature of these MOs differs markedly from those of the stoichiometric ones. As, V, and Mn atoms contribute partially to a large set of MOs, including the highest occupied and lowest unoccupied ones (HOMOs and LUMOs, respectively). The obtained results suggest that similar "magnetic" clusters may be of interest for the materials development for the future devices with integrated logic and storage capabilities.

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