CONDENSED-STATE PHYSICS

ELECTRONIC STRUCTURE AND ENERGY RATIOS OF Ni₃Al Clusters in TiNi Nanoparticles with an Impurity Al Atom

V. S. Demidenko, N. L. Zaitsev, A. V. Nyavro, and T. V. Menshchikova

The scattered-wave method is used to calculate electron spectra of central Ni₈Ti, Ti₈Ni, and Ti₈Al nanoclusters in nanoparticles of (Ni₂₆Ti₆₄)Al₁ and (Ti₂₆Ni₆₄)Al₁ alloys in the B2 structure. The single Al atom is shown to have a better chance for accommodation on the titanium sublattice because of high binding energy.

INTRODUCTION

Vigorous development of nanotechnologies has generated a need for theoretical and experimental investigations into the relationship between the structure and properties of nanoparticles containing a small number of atoms. The continually improved methods required for this purpose enable fundamental scientific concepts formulated in the past to be complemented and refined [1] and the physical-chemical properties of nanoparticles showing promise for practical applications to be revealed.

In this regard, of particular interest, in our opinion, are investigations into the structure of various nanoparticles and its dependence on the number of constituent atoms and into the properties of nanosized objects with heterogeneous structure. For example, the effect of the amorphous Si nanoparticle size on the optical properties of the material was studied by the tight binding method [2] to show drastic changes in the properties as compared with the bulk state. It was found in the framework of electronic density functional theory that magnetism was suppressed as the number of Si atoms in SiₓFe clusters was increased [3]. What is more, analysis of the cluster energy suggests their stability. A combination of calculations based on the semi-empirical molecular-orbital method and that of molecular dynamics revealed that the structural stability of nanostructured boron nitride is largely determined by twinning [4]. Using methods of the electronic density functional and molecular dynamics, it was shown that addition of a single Li, Na, Mg, or Al impurity atom to a Si₁₀ cluster impaired its stability, whereas addition of C, B, or Be enhanced the cluster stability in a more efficient way than that of a Si atom did [5].

Combining well-known methods and developing new ones [6, 7] appear to be a marked trend observed in investigations into nanoclusters, which allows for a most complete account of the special features of their electronic structure. The need for an integrated approach is underlined in [8], where electron spectroscopy, infrared absorption, and transmission electron microscopy were used to study the dependence of the valence-band structure on the gold nanoparticle size and traditional approaches were shown to fail to explain this effect.

The use of methods of multiple-scattering theory to represent real space for an analysis of the relation between the cluster size and shape and the scatterer characteristics occupies a special place in investigations into properties of small particles [9]. Due to high accuracy of the calculations, the approaches relying on the multiple-scattering theory enable the quantum mirage phenomenon to be investigated on the basis of, say, the first principles. In the case under consideration, the exchange interaction length for magnetic adatoms was several tens of microelectronvolts [10].

Examples of studying heterogeneous nanoparticles are cited in [11, 12]. In the former work, the pseudopotential method and the electronic density functional were used to investigate the properties of the metal-carbon nanotube contact.
In the latter work, the properties of anion defects in an Au cluster with $D_{3d}$ structure were examined. It was shown within the multiple-scattering theory [13] that the vacancy wind force during electric migration is decreased due to multiple-scattering effects if the diffusing atom “sees” an isotropic vacancy distribution. For a distribution typical of a grain boundary, the force is increased.

As more experimental and theoretical data become available, certain generalized conclusions are made. For instance, it is argued in [14, 15] that even very small systems containing several tens of atoms have magic structures with a high probability of being realized in practice. The structural stability of such systems essentially depends on the thermodynamical and kinetic factors, and not just on their energy and geometry. Since the main body of the research deals with materials where localized electronic $d$ states play a negligible role in the formation of the electronic-energy structure around the Fermi energy, the generalization should be made with caution.

As is shown in [16–18], the energy difference between crystal structures of transition metals and alloys is determined ultimately by the difference between the spectra of valence $d$ electrons. This kind of results was obtained in [19] for large nanoclusters containing atoms with equivalent potentials in a parametric model allowing for an analytical solution. In this connection, it is necessary to consider in detail the effect of the $d$ states on the energy of the ground state of nanoparticles whose structure is based on atoms of transition elements.

To perform such an analysis, taking, as the case in point, nanoparticles formed by Al, Ti, or Ni atoms, use was made of the scattered-wave method [20–22] being the simplest realization of principles underlying the multiple-scattering theory for objects with a finite number of scatterers. Notably, the accuracy of the scattered-wave method compares well [23] with the related Korringa–Kohn–Rostoker (KKR) method that has repeatedly proved its efficiency with respect to large cyclic systems [24, 25]. Thus, realization of the scattered-wave method enables the problem of revealing the relation between the special features of electron spectra of clusters and their energy ratios to be solved.

**NANOSTRUCTURAL CHARACTERISTICS AND COMPUTATIONAL PROCEDURE**

The scattered-wave method was used to calculate the electron spectra of Ni$_8$Ti, Ti$_8$Ni, and Ti$_8$Al nanoclusters at the center of (Ni$_{26}$Ti$_{64}$)Al$_1$ and (Ti$_{26}$Ni$_{64}$)Al$_1$ nanoparticles containing 91 atoms each in the $B_2$ structure. Interaction of the clusters with the environment was accounted for by addition of the potential of each of the nanocluster atoms to its increment formed at each site due to nuclear and electronic charges of 82 atoms of the nanoparticle.

The atomic spacing in a nanocluster in the structures under consideration required for calculations of the electron spectra was found from known lattice parameters of solid metals and compounds [26, 27]. As the shortest atomic spacings in bulk compounds coincide very closely (within several percent) with the sum of atomic radii of the components for a lattice with a structure realized in the ground state, the ratio of $m^t$-sphere radii for the nanocluster compounds was determined from the ratio of the atomic core radii of constituent elements reported in [28, 29]. The calculations show that the results obtained are essentially unaffected by a change in the $m^t$-radii and lattice parameter of the nanocluster in the neighborhood of values (~10%) found from the data for the ground state of the bulk materials.

With allowance made for quick convergence of the series in the orbital quantum number $l$ (as in the KKR method [24]), the expansion of the wave function used in the scattered-wave method is restricted to $l = 2$. The wave function for Al was calculated in the approximation adopted in [30], whereas the wave functions for Ti and Ni atoms were estimated with an exchange potential of the form given in [31]. The same exchange-correlation term was used to construct the nanocluster potential. In the latter calculation, the initial electron configuration of the valence shells of Ti and Ni atoms was replaced by an overfilled $3d^{10}4s^1$ shell. This configuration was chosen on the basis of the following considerations. Test calculations for Ti compounds with $d$ metals show that the ground atom configuration causes both excessive narrowing of energy intervals and a wide disparity between the difference in the centroids of these intervals and that observed in the bulk compounds [32]. Similar effects were revealed in the case where the exchange-correlation potential [31] was replaced by the exchange potential [20]. By and large the set of atomic electron configurations, atomic spacings in a nanocluster, and $m^t$-sphere radii chosen is assumed to provide a result approaching that obtainable in the self-consistent version of the scattered-wave method.