

VIBRATIONS OF TETRAHEDRAL Co AND Cu CLUSTERS ON Cu(111) SURFACE

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The epitaxial thin-film growth of Co on Cu substrates has been studied extensively during the last years. Because of the giant magnetoresistance observed in Co/Cu multilayer systems and its sensitivity to the atomic-scale morphology, extensive experimental studies have been devoted to their growth. These studies have revealed a variety of growth modes [1-6]. At the initial stages of growth some of the deposited Co atoms can exchange with Cu substrate atoms. This atomic exchange in conjunction with its coverage dependence leads to three different adatom species on the surface: substitutional Co, on-surface Co, and on-surface Cu, which can form compact clusters [1,6]. Numerous theoretical investigations have also been performed to study atomic structure as well as energetic and magnetic properties in Co/Cu system. Using density-functional theory calculations possible equilibrium structures for a monolayer coverage of Co on Cu(001) were analyzed [2]. Atomistic processes involved in the growth of Co on Cu surfaces were studied by employing static energy calculations and accelerated molecular dynamics simulations [7]. The interplay between structure and magnetic properties of small cobalt clusters on Cu surface were investigated by *ab initio* and tight-binding calculations [8]. Despite important role that vibrational properties of small clusters play in understanding of many phenomena such as adsorbate diffusion, island and film growth significantly less attention was paid to study adsorbate and cluster vibrations on Cu surfaces. Recently vibrational properties of a single adatom [9-11] as well as of a dimer, and trimer of Co on low-index Cu surfaces [11,12] have been thoroughly studied by using tight-binding second moment approximation interatomic interaction potentials. It was shown that structural and vibrational properties of the Co clusters strongly depend on the substrate orientation and the cluster size.

The simplest 3D clusters that can be formed in this system, tetrahedral Co₄ and Cu₄ clusters are considered in the present work. We study vibrational properties of these clusters on Cu(111) surface by using many-body interatomic potentials developed within tight-binding second moment approximation (TB-SMA) [13,14]. To determine the equilibrium atomic structure of free and supported clusters standard molecular dynamic technique based on the TB interaction potentials is applied. To simulate a semi-infinite Cu(111) surface with an adsorbed cluster a thin-film model of a two-dimensional periodic slab consisting of 31 atomic layers of Cu(111) with 5×5 supercell to exclude direct cluster-cluster interaction is used (see Fig. 1). The chosen thickness prevents interaction between two opposite surfaces of the copper film. The calculations of vibrational spectra are carried out by the dynamical matrix method. Diagonalizing the matrix gives the eigenfrequencies and the polarization vectors of vibrations. The local vibration densities of states were obtained by projecting these eigenmodes onto atoms of the cluster or the substrate in a given (*x+y* or *z*) direction. We also have done calculations of the equilibrium structure and vibrations of the free standing Cu₂ and Co₂ as well as Cu₄ and Co₄ clusters. The calculated Co₂ and Cu₂ bond lengths, binding energies, and the stretch mode frequencies are in close agreement with available experimental data.

In Fig. 2 we show the calculated local density of states (LDOS) for the Cu_4 (a) and Co_4 (b) cluster atoms and for the first and second Cu(111) layer atoms. Analysis of equilibrium structure of the adsorbed tetramers shows that in the case of Cu_4 the interaction with Cu(111) substrate leads to weakening Cu-Cu bonds within cluster while for the Co cluster interaction with the substrate affects only the Co-Co bonds between atoms closest to the surface. In both cases the clusters lose a high symmetry tetrahedral shape, which they have in a free standing state. The interaction of the Co and Cu clusters with the substrate leads to vibrations which correspond to translational and rotational degrees of freedom of the free clusters. These frustrated translation and frustrated rotation modes are in-plane polarized and lying in a low-frequency region. The frequencies of these modes in the Co cluster are ≈ 2 meV higher due to the stronger Co-Cu interaction in comparison with the Cu-Cu one. The vibrational modes of the free Cu_4 upon its adsorption on the Cu(111) surface mix with Cu bulk phonons and become almost delocalized. Contrary to that, in the Co_4 cluster on the surface the high frequency modes remain strongly localized and mixed with the nearest neighbor atoms vibrations only. Like vibrational modes of smaller Co clusters on low-index Cu surfaces, the highest frequency vibration of the Co_4 cluster splits due to different interactions with certain groups of nearest neighbor atoms of the substrate.

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Figures:

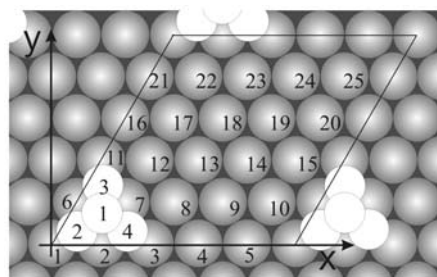


Figure 1 The atomic structure for adsorbed Cu_4 (Co_4) cluster on the Cu(111) surface. The computational 5×5 supercell is indicated by a rhombus, $x = [\bar{1}10]$ and $y = [11\bar{2}]$.

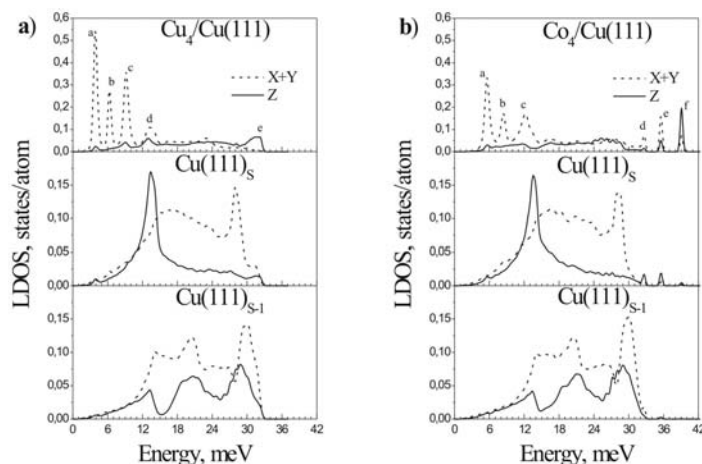


Figure 2 Local density of vibrational states for a tetrahedral clusters: a) Cu_4 and b) Co_4 as well as for the Cu(111) surface (S) and subsurface (S-1) atoms.