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Two-dimensional condensation of atoms adsorbed on a hexagonally packed crystalline surface: CVM theory incorporated with three kinds of sites

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Abstract

This paper presents a cluster variation theory of physical adsorption of atoms on a hexagonally packed crystalline surface. The surface provides three kinds of adsorption sites with different potential energies: two kinds of hollow sites and atop sites. The sites of each kind form a (1×1)-1/3 sublattice in the whole triangular lattice. Atoms exclude each other from first nearest neighbor sites because of their large size. The interaction energies between atoms are described by a Lennard-Jones $(12,6)$ potential. Thermal motion of atoms oscillating around their lattice sites is also incorporated through a cell model. The cluster variation method is applied to hexagon clusters of sites that overlap with each other at rhombus clusters of sites. We calculate the critical temperature of the two-dimensional condensation of Ar as a function of the lattice incompatibility between the substrate and the adsorbate in the range where the substrate lattice is nearly equal to or larger than the adsorbate lattice at zero temperature. Our calculations show quantitatively good agreement with experiment when the Lennard-Jones energy parameter of adsorbed Ar is reduced to 0.6–0.7 times the one of gaseous Ar. The critical temperature shows close parallelism with the apparent interaction energy between atoms at second nearest neighbor sites, which involves the vibrational free energy increment brought about by atoms surrounding at second nearest neighbor sites. The conventional statistical mechanical treatment that makes use only of one sublattice with the deepest potential is found to underestimate both the internal energy and entropy of the adsorbate, in particular at low densities.

Keywords: Equilibrium thermodynamics and statistical mechanics; Physical adsorption; Surface thermodynamics (including phase transitions); Noble gases; Halides; Insulating surfaces; Adsorption; Lattice; Phase transitions; Statistical mechanics

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1. Introduction

Hexagonally packed crystalline surfaces such as fcc(1 1 1) and hcp(0 0 0 1) surfaces have in general a low surface energy and then tend to be exposed to a gas–solid interface. These surfaces are widely known not only for metals but also for insulators and semiconductors such as CdI_2, $CdCl_2$ and MoS_2, and therefore they have aroused much interest in both fundamental science and technological applications. When a noble gas atom or a small molecule is physically adsorbed on such a surface, the most stable adsorption site is a hollow site right above the center of three surface atoms. The hollow sites are classified into two types, hcp site and fcc one, according as a substrate atom exists or does not exist in the second surface layer just beneath the site. These two types of sites have in general different adsorption potentials. The atop site on a surface atom also provides a potential minimum for an adsorbing gas atom, which is usually shallower than the hollow sites. These three kinds of sites are referred to as A-, B- and C-sites in order of the potential depth. All the sites of the three kinds constitute a triangular lattice and the sites of each kind compose a (1×1)-1/3 sublattice of the whole lattice. The sublattice made of C-sites (atop sites) is overlapped with and located right above the triangular lattice made of surface atoms.

Usually, adsorbed atoms cannot sit side by side on nearest neighbor (n.n.) sites because of their large size. Accordingly, most of adsorbed atoms occupy A-sites in many cases to form the 1×1 structure when the atoms complete a monolayer in registry with the substrate surface. This is the reason why many authors simplified the problem by making use only of the A-sublattice. However, such treatment does not always provide sufficiently accurate calculations, as shown by previous studies of adsorption on a honeycomb lattice [1,2].

In this paper, we develop a statistical mechanical theory on the basis of a more complete model in which B- and C-sites are incorporated. At the limit of an infinitely high adsorption potential of the C-site, the model is reduced to a honeycomb lattice gas. Therefore, the model to be presented in this paper will be more general than honeycomb lattice gas models such as studied previously [1,2]. Adsorbed atoms will be assumed not to sit side by side at n.n. sites. To obtain sufficiently accurate results, we employ the cluster variation method (CVM) [3–7] as a tool of statistical mechanical treatment. The effect of thermal motion of adsorbed atoms oscillating around their lattice sites is also involved in the model via an appropriate cell model.

Our theory will be applied to the two-dimensional condensation of atoms adsorbed on hexagonally packed crystalline surfaces. We try to reproduce an empirical relationship between the critical temperature and the lattice incompatibility between the substrate and the adsorbate, which was experimentally observed by Larher and coworkers [8,9] for Ar adsorbed on various lamellar dihalides such as CdI_2 and $CdCl_2$. These dihalides belong to the hexagonal crystal system and tend to expose their hexagonally packed halide ion arrangements to crystal surfaces. One of the present authors [10–12] once tried to analyze their findings statistical mechanically, but only in a qualitative manner where crude statistical mechanical approximations were employed with neglect of B- and C-sites. We revisit the same problem to quantitatively reproduce the experiment by use of the sophisticated theoretical model for the case where the substrate lattice spacing is nearly equal to or larger than the spacing of Ar atoms at zero temperature.

This paper is organized as follows. The next section presents our model. In Section 3, our theory will be developed in the framework of CVM. In Section 4, calculated results will be shown and compared to the experimental results reported by Larher and coworkers [8,9]. Section 5 will summarize this work.

2. Model

2.1. Interaction energies

Consider a triangular lattice composed of $3N_0$ lattice sites. Each lattice site can accommodate a single atom. The lattice is decomposed into three triangular sublattices, called A-, B- and C-sublattices. A lattice site that belongs to the A-sublattice