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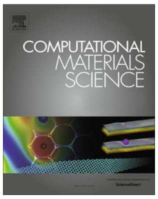

Study of peculiarities of the thermal expansion of zirconium thin films by molecular-dynamics simulation

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ABSTRACT

The peculiarities of thermal expansion of *bcc* and *fcc* zirconium films with (100) and (110) crystallographic orientations are studied at a constant zero pressure by the molecular dynamics (MD) method with a many-body interatomic interaction potential obtained in the embedded atom model. It is shown that after relaxation the cubic lattices become tetragonal (*bct* and *fct*), and for the *fct* films the linear coefficients of thermal expansion in the film plane have a negative value in a wide temperature range. The total and local vibrational density of states (VDOS) polarized along the x, y, z axes is calculated for the surface and interior layers of *bct* and *fct* Zr films as a function of temperature. It is shown that the peculiarities of the behavior of the vibrational density of states of surface atomic layers manifest themselves in the anisotropy of the changes of the film lattice parameters with temperature variation. A decrease in the lattice parameters with increasing temperature is observed in the directions where there occurs a softening of the local vibrational modes.

1. Introduction

In recent years, an ever increasing number of papers have been devoted to the study of so-called "negative" materials having negative coefficients of thermal expansion [1–4]. In 1996 the research team led by John Evans published the paper [1] in which a negative coefficient of thermal expansion (CTE) was found for the ZrW_2O_8 ceramics in a wide range of temperatures from 0.3 K to 1050 K. Later many other compounds with similar properties, named Negative Thermal Expansion (NTE) materials, have been discovered [5].

These materials with unusual properties are interesting not only theoretically, but also from an industrial standpoint. Materials with controlled thermal expansion can find several practical applications, such as switches and sensors, while materials with zero thermal expansion in a wide temperature range will be used in high-precision engineering. In instrument-making industry materials with strictly regulated values of linear CTE in specified temperature ranges of operation are in great demand. Recently the Evans team has created a material whose properties can be controlled throughout the thermal expansion range: from positive through zero to negative CTE [6]. The composite oxide Zr Mo_2O_8 is a well studied compound distinguished by a negative CTE, whereas the tin-containing analog of this cubic material, Sn Mo_2O_8, expands when heated. The authors of that paper state also to have demonstrated the possibility of introducing various amounts of zirconium into the lattice so that the obtained ceramic material can have a positive, negative or zero CTE. In essence the "positive" nature of the tin-containing material is balanced by "negative" zirconium, both metals being key elements of the same crystalline structure. Additionally, in Refs. [7,8] it was shown by inelastic neutron scattering that in NTE structures a softening is observed in the VDOS curve. Thus a negative thermal expansion coefficient is observed in materials which are in a metastable state (for example, near a structural transition), have a strongly anharmonic character of interatomic interaction, and/or a softening of the phonon modes is evidenced in the VDOS curve, which results in a negative value of the Grüneisen parameter.

Zirconium is known to be a strongly anharmonic metal. As we see, it plays a decisive role in the formation of negative CTE in the NTE structures. We believe, then, that the study of the thermal expansion of Zr nanofilms is an important task, because elucidation of the dependence of linear CTE on the temperature and film thickness will make it possible to reveal the peculiarities of the formation of thermodynamical properties of nanofilms and draw some conclusions about the influence of the surface structure on their properties. Clarification of the nature of special physical features of nanosystems is of interest for both fundamental problems of the condensed matter physics and possible practical applications.

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Earlier [9], we constructed a phase diagram Temperature-Thickness for zirconium films. This diagram presents the regions of final structures stable for no less than 1 ns, one time step being equal to 1 fs. Here we should mention some important points. Firstly, the size effect was detected. Two characteristic sizes may be noted. The first one is of 5 unit cells (u.c.) (~2 nm): up to this size the film just falls apart, and the second critical size is the film thickness of 17 unit cells (~6.1 nm) at which the mechanism and sequence of structural transformations change: from this size on the *bcc* (001) film remains stable in a certain temperature range. Secondly, what is especially important, structures not observed in pure Zr in the usual bulk state were found. These are *fcc* and orthorhombic structures. Recall that at atmospheric pressure only two phases are observed in Zr bulk samples: a high-temperature *bcc* phase, and an *hcp* phase found below 1136 K.

The studies performed in [9,10] have shown that the temperature of the $bcc \rightarrow hcp$ structural transition in zirconium films essentially depends on the thickness. The free surface can be considered as a structural defect favoring the formation of a new phase. Furthermore, the presence of the surface leads to a change in the total energy. All these factors contribute to the fact that in thin films (2–6 nm) the structural transformation from *bcc* to *hcp* is observed at temperatures above 1136 K. With increasing film thickness the transition temperature decreases. Thus, zirconium provides a possibility of studying the properties of a strongly anharmonic material existing in both stable and metastable states, in conditions close to structural transformations.

The main objective of the work was to study the effect of temperature on the properties of zirconium thin films. The MD method allows one to determine the thermodynamic and structural characteristics of a material under the conditions that are currently unfeasible in full-scale experiments. No experimental data on the thermal expansion of zirconium nanofilms are available in the literature. The molecular dynamics method makes it possible to determine the linear CTE in different crystallographic directions, namely, in the direction normal to the film surface, and in the plane of the film atomic layers, which allows the study of the film thermal expansion anisotropy. Furthermore, this method enables the investigation of physical characteristics, such as the lattice dynamics, separately for the surface and interior atomic layers of the film. In this work the MD method is used to study the peculiarities of thermal expansion of the zirconium thin films with cubic (*bcc*, *fcc*) crystal structures for different crystallographic orientations of the surface at a constant zero pressure. We also performed a comparison of the temperature behavior of the lattice parameters and vibrational density of states of surface and interior atomic layers, polarized both in the film plane and in the direction normal to the film surface.

2. Calculation method

The physical characteristics of zirconium films were studied by the MD method using the standard XMD package [11]. The many-body potential (#2) from Ref. [12] constructed within the embedded atom model [13] was chosen to describe the interatomic interaction in zirconium. In Ref. [12] it was shown that this potential allows one to obtain, to a high degree of accuracy, the *bcc* and *hcp* lattice parameters of zirconium, cohesive energy, elastic constants, melting temperature, and other physical characteristics. The bulk phonon dispersion curves calculated with this potential along the symmetrical directions of the Brillouin zone of *bcc* zirconium at different temperatures were obtained in our paper [14]. A comparison with the experimental data shows that the potential chosen allows one to reproduce the experimentally observed features of the Zr phonon spectrum including the softening of the transverse N-phonon with decreasing temperature, and so it may be successfully used in calculating vibrational and thermal characteristics of zirconium films.

In this paper we present only the vibrational density of states for bulk configuration ($24 \times 24 \times 24$ u.c.) *bcc* zirconium (see Fig. 1) as compared with the experiment [15]. As seen from Fig. 1, the positions of the main peaks are in good agreement with the experiment.

All simulations were carried out with a time step $\Delta t = 1$ fs. In simulations of the bulk configuration, cyclic boundary conditions, for simulations of the films, free boundary conditions were specified along the z axis. The film thickness along the z axis varied from $N_z = 5$ to $N_z = 30$ unit cells. In the x and y directions cyclic boundary conditions were used with $N_x = N_y = 24$ u.c. Thus we simulated thin films infinite in x, y, with free surfaces on the z axis. In all variants, the calculation started with the formation of a crystallite with perfect *bcc* or *fcc* structure and orientation of the film surface (001) or (110). The system was heated from an initial temperature of 50 K with a step $\Delta T = 50$ K. At each new temperature the system was held in the state of free evolution for no less than 50 ps. To calculate the lattice parameters and VDOS at the selected temperature, the system was additionally held for 50 ps, and only then the computation was carried out.

The total VDOS, $g(\omega)$, was calculated as the Fourier transform of the autocorrelation velocity function, the velocity was averaged over all atoms on an interval of 10 ps after a relaxation period of 100 ps at a given temperature:

$$g(w) = \int dt \frac{\sum_{i=1}^{N} \langle \mathbf{v_i}(t)|\mathbf{v_i}(0)\rangle}{\sum_{i=1}^{N} \langle \mathbf{v_i}(0)|\mathbf{v_i}(0)\rangle} \exp(iwt). \quad (1)$$

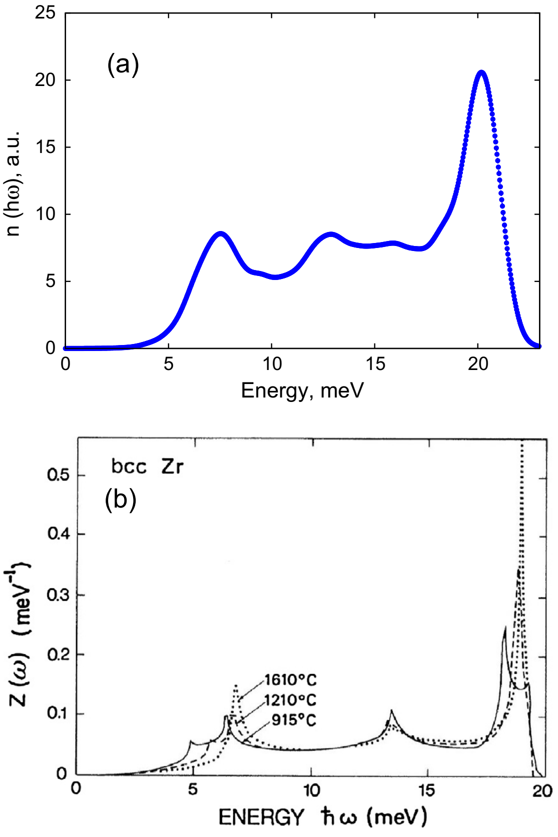

Fig. 1. Vibrational density of states of *bcc* Zr: (a) calculated for a crystallite with cyclic boundary conditions at $T = 900$ K; (b) experimental values [15].