Surface Science 679 (2019) 1–5

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Surface discrete breathers in Pt_3Al intermetallic alloy

P.V. Zakharov[a,b], E.A. Korznikova[c,*], S.V. Dmitriev[c,d], E.G. Ekomasov[e], K. Zhou[f]

[a] Altai State Humanitarian and Pedagogical University, Biysk 659333, Russia
[b] Altai State Technical University, Barnaul 656038, Russia
[c] Institute for Metals Superplasticity Problems of RAS, Ufa 450001, Russia
[d] National Research Tomsk State University, Tomsk 634050, Russia
[e] National Research South Ural State University, Chelyabinsk 454080, Russia
[f] Nanyang Technological University 639798, Singapore

A B S T R A C T

It is known that defect-free crystals can support spatially localized, large amplitude vibrational modes with frequencies outside the linear phonon spectrum. Such excitations are called discrete breathers (DB) or intrinsic localized modes. So far, for 3D crystals DB were considered only in the bulk. In the present molecular dynamics study, for the first time, we demonstrate that DB can be excited at the low Miller indices surfaces of the Pt_3Al intermetallic alloy. It is shown that properties of the DB depend essentially on the surface orientation and termination, as well as on DB polarization. The study of DB at crystal surfaces is important because they can localize energy of order of 1 eV, which can reduce the potential barrier for local structure transformation or a chemical reaction.

1. Introduction

Discrete breathers (DB) are high amplitude localized vibrational modes in perfect nonlinear lattices. They have been analyzed in the pioneering studies [1,2] that have initiated a great research activity summarized in the reviews [3,4]. Since the last decade, DB have been actively investigated in solid state physics and material science [5–28]. In experimental works DB are detected in crystals by measuring their vibrational spectra [6], but these results are still debated [7]. Experimental detection of DB in crystals is a challenging task because of their sub-nanometer size and short lifetime in presence of thermal fluctuations. That is why atomistic simulations are very useful in the study of DB properties in crystals [5]. With the help of molecular dynamics DB have been analyzed in pure metals [8–12], in model crystals with Morse interactions [13,14], in diamond [15], in graphene [16–20] and boron nitride [21]. First-principle simulations for DB in graphene confirm the molecular dynamics results [22]. A number of studies have been devoted to the crystals with A_3B composition with a big difference in the atomic masses of the components [23–28]. Such crystals possess a gap in the phonon spectrum and support DB with frequencies within the gap. Such DB is easy to excite since it is highly localized on a light atom.

It should be pointed out that DB are traditionally investigated in the bulk of crystals [5–18,21–28]. In some studies, vibrational modes localized at the end of a 1D chain are called DB [29–33], but rather they should be called localized surface modes or Tamm states [34–36], since DB by definition is a vibrational mode localized in a perfect lattice with translational symmetry. DB at the edge of a homogeneously stretched graphene nanoribbon were studied in [19,20] and it was shown that the configuration of such DB differs strongly from DB inside the graphene sheet [17,22]. Note that the DB at the edge of graphene sheet exists in a one-dimensional discrete medium, with the direction of translation along the edge of the sheet. By analogy, one can search for DB close to an atomically flat (singular) surface of a three-dimensional crystal. To the best of our knowledge, so far no attempts have been made to find near-surface DB for a 3D crystal.

Near-surface DB can contribute to the physics and chemistry of surface. They localize some energy which can reduce the potential barriers for structure transformations at the surface, for creation of surface crowdions [37,38] or voidions [39] contributing to surface diffusion [40–42]. DB can accelerate chemical reactions [43]. DB at crystal surface can be excited by external driving [44–48].

In the present work molecular-dynamic study of near-surface DB is carried out for Pt_3Al crystal.

2. Simulation details

We consider the model of Pt_3Al intermetallic alloy with $L1_2$ superstructure based on fcc lattice. Primitive translational cell of this crystal is shown in Fig. 1a. One of the four cubic sublattices is occupied by Al atoms (blue balls) and the other three by Pt atoms (brown balls).

Three surface orientations are considered with all possible terminations, as shown in Fig. 1b-f. Here large (small) balls show the atoms of the first (second) atomic plane. Surface translational cells are indicated. In Fig. 1b and Fig. 1c the surface is parallel to (100)

* Corresponding author.
E-mail address: elena.a.korznikova@gmail.com (E.A. Korznikova).

https://doi.org/10.1016/j.susc.2018.08.011
Received 24 May 2018; Received in revised form 17 July 2018; Accepted 17 August 2018
Available online 18 August 2018
0039-6028/

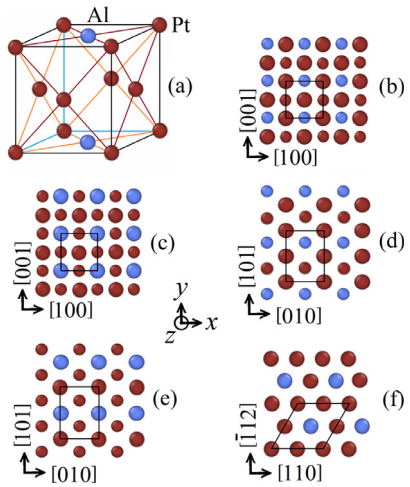

Fig. 1. (a) Primitive translational cell of Pt_3Al intermetallic alloy based on fcc lattice. One of four cubic sublattices is occupied by Al atoms (blue balls), while the other three by Pt atoms (brown balls). (b–f) Top views of the studied surfaces. Larger and smaller balls show the atoms in the first and second atomic planes, respectively. Surface translational cells are specified. Cartesian coordinate system used in the simulations is shown. (b,c) Surface parallel to (100) crystallographic plane terminated by Pt atoms and by atomic plane with composition PtAl, respectively. (d,e) Surface parallel to (110) crystallographic plane terminated by Pt atoms and by atomic plane with composition PtAl, respectively. (f) Surface parallel to (111) crystallographic plane. All (111) atomic planes have composition Pt_3Al. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

crystallographic plane. In the former case it is terminated by Pt atoms, while in the latter case the first atomic plane has composition PtAl. In Fig. 1d and Fig. 1e the surface is parallel to (110) crystallographic plane and it is terminated by Pt atoms and by the atomic plane with composition PtAl, respectively. In Fig. 1f the surface is parallel to (111) crystallographic plane and the surface atomic plane has composition Pt_3Al.

The number of atoms in the system varied from about 10^5 to 2×10^5, depending on the surface crystallographic orientation. Relatively small computational cells are sufficient for the present study since DB is highly localized on single Al atom with neighboring atoms having much smaller oscillation amplitudes.

Periodic boundary conditions are applied in x and y directions and free surfaces parallel to xy-plane are modeled on both sides of the computational cell.

The interatomic potentials for the Pt_3Al intermetallic alloy were generated by the use of the method proposed by Zhou [49], which is based on the embedded atom method (EAM) [50]. Potentials used in this study are fitted to reproduce basic properties of the alloy such as lattice constant, elastic moduli, sublimation and defects formation energies, demonstrating satisfactory agreement with the experimental values. Details of the interatomic potential development and testing are given in [24].

Homemade software is used for simulations. The equations of atomic motion are integrated with the use of the Störmer method of order six with the time step of 0.5 fs. This symplectic method belongs to a wider family of integrators, as described in [51]. For a typical numerical run relative reduction of total energy of the system was not greater than 10^{-8}.

Before excitation of DB the crystal structure with free surfaces is relaxed with the use of the steepest descent method to obtain equilibrium surface structure.

All simulations are done at 0 K, i.e., the effect of thermal fluctuations is not taken into account.

An important problem is to find initial conditions that result in excitation of a DB. Pt_3Al intermetallic alloy supports several types of DB in the bulk [26,27]. In this study we consider the simplest one, which is localized on single Al atom and shows the soft type anharmonicity, i.e., its frequency decreases with the amplitude, being within the gap of phonon spectrum (from 5.82 to 8.45 THz). Such highly localized DB can be easily excited in the bulk by initial displacement of one Al atom with initial zero velocities for all atoms in the computational cell. The magnitude and direction of the initial displacement define the amplitude and polarization of the DB, respectively. Pt_3Al crystal supports gap DB in the bulk polarized along ⟨100⟩ crystallographic direction [25–27]. An attempt to excite a DB in the bulk with another polarization results in a very rapid decay of the vibrational mode or in a spontaneous change of oscillations to ⟨100⟩ polarization.

Note that in the present study we always choose Cartesian coordinate system with xy plane parallel to the surface and z axis normal to the surface, as shown in Fig. 1. Attempting to excite a DB near crystal surface, we apply initial displacement of different magnitude to one Al atom closest to the surface in x or y direction parallel to the surface or in the direction normal to the surface (along z axis). The direction of initial displacement defines DB polarization. All other atoms have zero initial displacements and all atoms have zero initial velocities. If the amplitude and direction of the initial displacement are chosen properly, a long-lived vibrational mode is established after a short transient period. We then measure the frequency and energy of the DB.

3. Results and discussion

3.1. (100) surface orientation

For the surface parallel to (100) plane two surface terminations are possible: the first atomic plane has (i) only Pt atoms (Fig. 1b) and (ii) equal amount of Pt and Al atoms (Fig. 1c). In the relaxed crystal, the interplanar spacing for the near-surface planes is different from the value in the bulk, as shown in Fig. 2a by triangles for Pt termination and by circles for PtAl termination. In the former (latter) case the interplanar distance near the surface is smaller (larger) than in the bulk.

Firstly we consider the case of Pt-terminated surface. If an initial displacement along x or y direction is given to a Al atom closest to the surface, a long-lived DB is excited. Lifetime of such DB can reach up to a few ns, which is above 10^4 oscillation periods. DB lifetime is defines as the time when its energy becomes 1/3 of the energy given to the system at $t = 0$. In our simulations there are two major reasons limiting DB lifetime. First is the use of very simple and thus rather poor initial conditions that produce not a DB but a quasi-DB [52]. Second reason is the initial energy burst produces by the poor initial conditions and constant energy radiation from quasi-DB. This emitted energy plays a role of thermal fluctuations that affect DB dynamics. Frequency and total (kinetic plus potential) energy of the DB as the functions of DB amplitude are shown by triangles in Fig. 2b and c, respectively. Horizontal dashed lines in Fig. 2b show the lower and the upper edges of the gap in the phonon spectrum of the crystal, 5.82 and 8.45 THz, respectively. The spectrum was calculated for the bulk crystal and it does not take into account the effect of the surface. DB amplitude can exceed 0.8 Å. DB frequency reduces with its amplitude revealing the soft type anharmonicity of this vibrational mode, and it lies within the gap of the phonon spectrum. DB energy can reach up to 2 eV. It turns out that the near-surface DB polarized along x or y direction has properties close to the DB in the bulk.

An interesting phenomenon was observed when Al atom closest to the surface was excited by initial displacement along z axis (normal to the surface). In a few picoseconds the vibrational energy of this atom was given to the Al atom just below the excited Al atom. This process is shown in Fig. 3, where displacements Δz as the functions of time are presented for the initially excited Al atom (dashed line) and for the Al atom below the excited atom (solid line). This process can be regarded as DB migration from the surface deeper into the bulk. After the DB vibrating along z axis moves deeper into the crystal, its properties