Analysis of the possibility of excitation of soliton-like waves in crystals using the ab initio method and molecular dynamic simulation

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Abstract. In this article, using the first-principle approach and the method of molecular dynamics, the authors investigate the properties of a Pt₃Al crystal with a view to the possibility of the existence of such waves of soliton-like waves as discrete breathers. Methodical aspects of crystal models building are presented, with the analysis of the advantages and disadvantages of each method. Such crystal properties as the density distribution of phonon states, dispersion curves, and electron density distribution are studied. Based on the density functional theory, it is shown that the spectrum of the crystal does not have a through band gap, however, along the <100> directions, it is possible to excite high-amplitude long-lived modes on Al atoms. The results indicate the benefit of the concept of discrete breathers in the investigated crystal.

1. Introduction

A soliton is a structurally stable solitary wave propagating in a nonlinear medium [1]. Such objects of the nonlinear world are widely used in various systems, starting with optical waveguides and ending with DNA molecules. Nowadays, there are a huge number of different types of solitons, as well as approaches to their classification [2-5]. The environments with translational symmetry are of particular interest, for example, crystal structures used in electronics, the space industry and high-tech manufacturing. Until recently, the possibility of the existence of soliton-type waves in such systems has not been strictly mathematically proved. However, in the works [6, 7], it was shown that different solitons can exist in discrete systems.

A wide interest is a special type of soliton - a discrete breather, named by analogy with the breather observed in continual media. Discrete breather is a spatially localized mode of large amplitude in a nonlinear discrete medium with translational symmetry [8]. Interest in this object increased when the first experimental results were obtained, which allowed judging the contribution of such solitons to the properties of crystals, such as heat capacity, thermal conductivity, superplasticity, and others [9–11]. Many articles were devoted to discrete breathers, in particular, the review [8]. A necessary condition for the existence of discrete breathers with a soft type of nonlinearity [8] is the nonlinearity of the medium and the substantial mass spread of the alloy components, more than 4 times, this causes the presence of a band gap in the spectrum of the crystal. The studied data properties are the purpose of this work.

To search for the possibility of the existence of such objects in various environments, computer simulation is the most popular, because of its low cost and the possibility of widely varying experimental...
conditions. In addition, the use of these methods is due to the fact that such objects at the micro level have a relatively short lifetime, a series of several hundred lattice oscillation periods. Among the methods of computer simulation used to study such objects in crystals, the method of molecular dynamics, based on solving differential equations of motion of each particle of the model, is the most widely used. This method has undoubted advantages: the simplicity of building a model, high count rate, a wide range of system parameters that can be controlled and measured. This method is not without flaws, the main of which is the choice of the interatomic interaction function, which does not always correctly describe the interaction of the particles of the system in comparison with the full-scale experiment. The quantum mechanical approach is devoid of these shortcomings, but it is extremely demanding of computing power. Currently, there are a number of papers [12, 13], where discrete breathers are simulated on the basis of the quantum mechanical method. In particular, such objects are considered in graphene and graphs, but the models used are not large in size and represent a model of a 2D structure. The authors chose for studies a 3D model of an alloy of composition A₃B with FCC structure, using the example of Pt₃Al.

Platinum alloys are used in many areas of science and technology. They are heat resistant and resistant to corrosion, are promising for microelectronics. In a number of works the possibility of the existence of discrete breathers in a given crystal presents using the method of molecular dynamics. [14, 15]. Next, the authors describe in more detail the molecular dynamic and quantum mechanical models of crystals.

2. The model and the experimental technique

The appearance of the models is shown in Figure 1. Due to the computational capabilities, the molecular dynamics model was larger than the quantum mechanical one.

The molecular dynamic model under consideration is a bulk FCC crystal of A₃B stoichiometry, using Pt₃Al as an example, which contains 52·10³ particles, interacting through the potential obtained by the immersed atom method (EAM potential) [16]. In computational chemistry, the model of a submerged atom is used to approximate the description of the interaction energy between two atoms. The choice of potential and the validity of its use for a specific task is an important step in modeling. The total energy E of a crystal can be expressed as:

\[ E = \frac{1}{2} \sum_{i,j \neq j} \psi_{ij}(r_{ij}) + \sum_i F_i(\rho_i). \]  

where \( \psi_{ij} \) represents the pair energy between atoms \( i \) and \( j \) separated from each other by the distance \( r_{ij} \), and \( F_i \) is the energy of the pair attachment associated with the inserted atom \( i \) in the local location with the electron density \( \rho_i \). Electronic density can be calculated by the formula: \( \rho_i = \sum_{j \neq i} f_j(r_{ij}), \) where \( f(r_0) \) is the electron density of the region of atom \( i \) located at a distance \( r_j \) from the atom \( j \). Modeling was done using LAMMPS package[17].

The quantum mechanical model was built using the Quantum Espresso package [18]. In view of the complexity of the calculations, the model contained 30 atoms. The program is based on the Kohn – Sham density functional theory for the exchange energy and correlation energy. This concept is based on the three-dimensional electron density distribution function \( n(r) \), on which natural restrictions are imposed:

\[ n(r) \geq 0, \int n(r) d^3r = N_e. \]  

The Cohn-Shem equation has the form:

\[ -\frac{\hbar^2}{2m_e} \nabla^2 \varphi_j(r, \mathbf{s}) + v_{KS}(r) \varphi_j(r, \mathbf{s}) = \varepsilon_j \varphi_j(r, \mathbf{s}), \quad j = 1..N_e \]  

where \( \varphi \) - single-particle wave functions, \( r \) corresponds to the coordinate, and \( \mathbf{s} \) corresponds to the electron momentum.
Figure 1. Volumetric view of models: (a) by the method of molecular dynamics, (b) the ab initio method.

The program solves the problem for self-consistent potential. The Bloch functions of electrons in a crystal are sought in the form of an expansion in a system of basic functions, which are plane waves. Approximation of the pseudopotential can significantly reduce the number of basis plane waves in the decomposition of electronic wave functions.

3. The results and the discussions

For the described models, the following actions were carried out: relaxation of the structure with the search for a state with a minimum of energy, calculation of the density of phonon states of the system. For the quantum mechanical model, the dispersion curves and the electron density distribution near the Al atom in the equilibrium position and at its displacement were additionally calculated. These properties of crystals are decisive for the existence of discrete breathers [8]. Their analysis will make it possible to conclude that such soliton-like waves exist in the material under consideration.

Figure 2. (a) Dispersion curves and density of phonon states of a Pt₃Al crystal, obtained by the first-principles method, (b) density of phonon states of a Pt₃Al crystal, obtained by the method of molecular dynamics.
When solving the problem using the molecular dynamics method, the LAMMPS software package was used, which includes the necessary procedures for these purposes, based on the Fourier transform of the autocorrelation functions of atom displacements with time. Figure 2b shows the density of phonon states of a crystal calculated earlier in the work [14], where the forbidden band is clearly seen in the spectrum of the crystal. The available data on the spectrum of this crystal, obtained by other methods, differ from this result [19], therefore, calculations are made from first principles (Figure 2a).

Figure 2 shows that there is no pronounced gap in the phonon spectrum, however, there are areas along separate directions where localized oscillations are possible, in particular, along the [100], [010], [001] directions. The discrepancies with the molecular dynamic model are associated with the impossibility of taking into account the electron density distribution in it. Further, its calculation is made, shown in Figure 3.

![Figure 3](image)

**Figure 3.** (a) The electron density distribution near the Al atom in the equilibrium; (b) position and at a shift by 0.5 Å along the [100] direction.

The existing asymmetry of the electron density of the Al atom with significant deviations from the equilibrium position leads to the absence of the possibility of the existence of high-amplitude localized oscillations along close-packed crystallographic directions. This is not an obstacle for oscillations along unpacked directions, as evidenced by the presence of corresponding regions in the phonon spectrum of the crystal.

4. **Conclusion**

The calculated properties of the Pt$_3$Al crystal using the ab initio method and the molecular dynamics method showed some discrepancy due to the fact that the molecular-dynamic model does not take into account the distribution of electron density with large deviations of atoms from the equilibrium position. This manifested itself in the absence of a wide band gap in the phonon spectrum of the crystal. However, the revealed features of the spectrum are in good agreement with the results of other researchers and allow speaking about the possibility of the existence of slotted discrete breathers only along certain directions of crystals, in particular, along the direction of type <100>. These results do not contradict the available data and can be useful in creating materials with unique properties, in the design of nanomaterials and the development of new technologies based on them.

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