Theory and molecular dynamics simulations of intrinsic localized modes and defect formation in solids

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Abstract

Molecular dynamics (MD) simulations of recoil processes following the scattering of x-rays or neutrons have been performed in ionic crystals and metals. At small energies (<10 eV) the recoil can induce intrinsic localized modes (ILMs) and linear local modes associated with these modes. As a rule, the frequencies of such modes are located in the gaps of the phonon spectrum. However, in metallic Ni, Nb and Fe, due to the renormalization of atomic interactions by free electrons, the frequencies mentioned are found to be positioned above the phonon spectrum. It has been shown that these ILMs are highly mobile and can efficiently transfer a concentrated vibrational energy over large distances along crystallographic directions. If the recoil energy exceeds tens of eVs, vacancies and interstitials can be formed, which are strongly dependent on the direction of the recoil momentum. In NaCl-type lattices the recoil in (110) direction can produce a vacancy and a crowdion, while in the case of a recoil in (100) and in (111) directions a bi-vacancy and a crowdion can be formed.

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1. Introduction

A number of important, for various applications, phenomena in solids are governed by atomic motions, which are characterized by large displacements and strong nonlinear forces. The radiation damage due to the production of defects of the irradiation of solids by neutrons, x-rays and other high energy particles in fusion and nuclear reactors may serve as an example. Here, in addition to initial, high energy cascade damage, the definitive result is essentially determined by the final stage of the damage which results from the collisions with particles of lower energy. In this article we investigate this final stage characterized by the moderate (\(\leq 100\) eV) recoil energy of collision \(E_R\). If \(E_R < 10\) eV (atomic velocities smaller than the phonon velocities), one can expect the creation of intrinsic localized modes (ILMs, also known as vibrational solitons, breathers, quodons) [1–3].

In [4, 5] an analytical theory of ILM was developed and associated with them, linear local modes (LLMs) were predicted. The latter manifest themselves as a modulation of ILMs amplitudes [6]. Recently, the existence of LLMs has been confirmed experimentally [7]. To investigate the localization and the transport of vibrational energy in a form of immobile and mobile ILM, we performed numerical simulations in metals. Here ILMs may exist only if their frequency is positioned above the phonon spectrum, which assumes atomic interactions with rather small odd anharmonicity. Our simulations showed that in some metals (Ni, Nb, Fe) such high-frequency ILMs are possible due to the screening of the short-range ion–ion interaction by the conducting electrons [8]. We have found that these excitations may have rather large energy and they can move over large distances along crystallographic directions in the lattice.

We also studied the evolution of the lattice excitations induced by the recoil processes following the scattering of neutrons or x-rays in crystals at recoil energies \(10 < E_R < 200\) eV, i.e. in the range where the vacancies and interstitials can be formed. We numerically simulated the formation of these defects in ionic crystals in dependence of energy, direction of the recoil momentum and of the atomic (ionic) masses of the crystal. In particular, it was shown that the defect pair, bivacancy + crowdion, can arise in NaI as a result of the great anion–cation mass difference. The long-range forces were partially taken into account in the simulations and we found that they can affect the behaviour of the crowdion-type defect created at recoil.
2. Self-consistent theory of intrinsic localized modes (ILMs) and linear local modes

In [4] a theory of ILMs is proposed, which is based on the consideration of small deviations. The latter satisfy the self-consistent linear equation \( \ddot{\alpha}_n = -\sum_{n'} \left( D_{nn'} + w_{nn'} \right) \dot{\alpha}_{n'} \). Here \( D_{nn'} \) is the dynamical matrix of the lattice in harmonic approximation and \( w_{nn'} \) is its perturbation by an ILM. If we take an ILM in the form \( u_L(t) = A_n \cos(\omega_L t) + O \) (the term \( O \) describes small higher-order harmonics), then the self-consistency condition reads \( \alpha_n = \zeta A_n \sin(\omega_L t) \), where \( \zeta \) is a small parameter (note the phase shift \( \pi/2 \) of the deviations with respect to the ILM). For such \( \alpha_n \) one gets

\[
\dot{w}_{nn'} = 2\langle \sin^2 \omega_L t \partial^2 V_{anh}/\partial u_n \partial u_{n'} \rangle. \tag{1}
\]

Here \( \langle \ldots \rangle \) is the averaging over the vibrational period (the explicit equations for \( w_{nn'} \) are given in [4]). The solution of the equation for \( \alpha_n \) reads

\[
\alpha_n = \alpha_0 \tilde{G}_n / \tilde{G}_{00}. \tag{2}
\]

\( \tilde{G}(\omega) = (I - G(\omega) w)^{-1} G(\omega) \).

Equation (2) is a self-consistent equation which can be solved selecting \( A_n \) and \( \omega_L \), step by step. The theory has been checked by numerical simulations of ILMs in monatomic and two-atomic chains [4, 5] (see figure 1) and it has been applied for alkali-halide crystals [9]. Analogously, one can also consider the effect of an ILM on the rest of the small vibrations (phonons) in the lattice [6].

3. Mobile ILMs with the frequency above the phonon spectrum

In [8] we derived a critical parameter for the ILMs existence: \( \tilde{k} = 3k_4k_2^2/4k_3^3 \) (here \( k_1 \) and \( k_4 \) are the cubic and quartic
anharmonic springs, $\ddot{r}_2 = M \dddot{v}/r_2^2$ is the mean elastic spring in the bulk crystal, $v$ is the longitudinal velocity of sound, $M$ is the mass of atoms, $r_0$ is the lattice constant). In insulators all standard pair-potentials, such as Morse, Lennard–Jones, Toda, Buckingham, Born–Mayer + Coulomb, used at the molecular dynamics (MD) simulations of ILMs, show a strong softening at the increasing of vibrational amplitudes ($\ddot{k} < 1$) due to large odd anharmonicity. As a result, the possible ILMs can only split down from the optical band(s) of the phonon spectrum into the spectral gaps. In metals, in the absence of the gaps mentioned the situation is very different. Here the condition $\ddot{k} > 1$ must be fulfilled to enable the position of a possible ILM above the phonon spectrum. We have shown that at least in some metals (Ni, Nb, Fe) $\ddot{k} > 1$, as the odd anharmonicity is strongly reduced due to the screening of the ion–ion interaction by the conducting electrons, and ILMs can exist. This conclusion was verified by the MD simulations of the recoil-induced dynamics in these crystals.

Very stable and well mobile ILMs have been found in iron (the mobility of the ILM is determined by the momentum of the initial excitation). In our calculations we have used the latest embedded atom model potential found by Mishin et al [11] (www.ctcms.nist.gov/~checker/Fe.html). Two series of calculations were performed: (i) using the original program and (ii) applying a LAMMPS package. (LAMMPS [http://lammps.sandia.gov/] is a classical MD code that models an ensemble of particles in a liquid, solid or gaseous state using a variety of force fields and boundary conditions.) Both calculations fully agree with each other. In the case of the immobile ILM (figure 2) and small motion of ILM (figure 3) the cluster with $40 \times 40 \times 40$ iron atom cells was used for MD simulations; for an extended motion (figure 4) cluster $12 \times 12 \times 12$, prolonged in the (111) direction to have 200 atoms in the (111) chain, was used (total number of atoms 73 328). The full energy of the ILM, represented in figures 3 and 4, is 1.5 eV.

4. Molecular dynamics simulations of recoil-induced defects

We have also studied the recoil-induced dynamics of NaI and KCl crystals at recoil energies $E_R > 10$ eV. In this energy range the generation of vacancies and interstitials can be expected instead of ILMs. We performed MD simulations in the rectangular clusters, extended along the crystallographic axes (the main directions of the studied recoil momenta). Clusters contain 3000 atoms and have a length of $60a_0$ in the (100) direction or 60$a_1$ ($a_1 = \sqrt{2}a_0$) in the (110) direction ($a_0$ is the lattice parameter). The clusters were located in the infinite host lattice of immobile ions. In the cluster, direct integration of the equations of the atomic motion was carried out using the short-range forces (Born–Mayer + van der Waals) of [12], cut off at $8 < r < 9$ Å. Coulomb forces between all ions of the cluster were taken into account and the Coulomb interaction with the host (anharmonic forces) was calculated using the Ewald method. The approximation of nonpolarizable ions was used in simulations. Note that the present potentials differ from the model used in [10]. The latter generated unrealistic results at some recoil momentum directions. The change of the model potential also decreases the threshold of the defect formation in the (110) direction case.

The lowest defect creation threshold (recoil energy $E_R \approx 25$ eV) was found for the (110) direction of the recoil. In such a direction the recoil causes a cascade of collisions in the (110) chain of identical atoms. As a result, one can observe the creation of a vacancy and a crowdion in the chain (figure 5), the crowdion–vacancy distance increasing with $E_R$. At exact (110) direction, an intensive crowdion drift toward vacancy took place after a 35 ps interval, which caused the annihilation of the defect pair. At deviations of the recoil direction from the (110) direction, the momentum transfer was accompanied by strong focuson effects in the solid angles $\Omega \leq 0.1$ sr around the (110) axis (figure 6).

In the case of a recoil in the (100) direction, a single vacancy cannot be formed and the result strongly depends on

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**Figure 5.** Time dependence of the positions of the colliding ions in a NaI crystal $r_n(t) = n + u_n(t)/\sqrt{2}a_0$. Displacements are induced by the recoil of primary Na ion ($n = 0$) in the (110) direction with $E_R = 27$ eV.
the anion/cation mass ratio (figure 7). In KCl (mass ratio ~ 1) a transfer of the recoil momentum over great distances along (100) axis took place. As the sequence of interionic collisions changes the order of the ionic charges in the (100) atomic chain, the new configuration proved to be very instable, the ions returned to their initial positions and no metastable defect could arise (at least at the energies $E_R < 200$ eV). On the contrary, in the case of a large anion/cation mass ratio (~5.52 in NaI) cooperative collision processes took place in the (100) atomic chain accompanied by large-amplitude vibrations of light cations (figure 7).

As a result, a bi-vacancy near the primary ion position and an extended crowdion appeared in the chain. The crowdion was slowly drifting away from the bi-vacancy. The required minimal recoil energy exceeded almost four times the corresponding $E_R$ in the (110) direction case. According to [10] an analogous defect pair can also be created at the (111) recoil direction, the pair being more compact due to the less density of the ions in the corresponding chain:

$$r_n(t) = n + u_n(t)/a_0.$$  

We note that the long-range forces, created by the ion displacements in the host crystal, have not been taken into account in these calculations. In our mind, their inclusion does not produce any qualitative changes, as the defect formation is mostly governed by strong short-range repulsive forces. Nevertheless, some influence on the threshold energies and on the stability of the defects is possible.

5. Conclusions

In this article the results of our recent studies of the atomic motion in perfect crystals, caused by the local excitations of the crystal lattices with the energy less than 200 eV, are presented. At small energies ($<10$ eV) the excitation can induce ILMs (see e.g. [1–5]) and recently predicted in [6] and experimentally observed in [7] LLMs associated with these modes. Usually pair potentials in dielectrics show a strong softening with the increasing of vibrational amplitudes. Therefore, in these materials, the ILMs can only split down from the optical band(s) into a spectral gap of the phonon
spectrum, if such gaps exist in the crystal. However, in metals due to the screening of the ion–ion interaction by conducting electrons the ion–ion potentials may be very different as compared to the insulator cases. A checkup, provided by us, shows that in metallic Ni, Nb and Fe, due to renormalization of atomic interactions by free electrons, the ILMs with the frequencies positioned above the phonon spectrum can arise. It is shown that these ILMs are highly mobile and can efficiently transfer a concentrated vibrational energy over large distances along crystallographic directions. If the recoil energy exceeds tens of eV, the vacancies and interstitials can be formed, in a strong dependence on the direction of the recoil momentum. In the NaCl-type lattices the recoil in the (110) direction can produce a vacancy and a crowdion. However, in the case of a recoil in the (100) direction the single vacancy cannot be formed and the result strongly depends on the anion/cation mass ratio. In KCl (mass ratio ∼1) a transfer of the recoil momentum over great distances along the (100) axis took place. As the sequence of interionic collisions changes the order of the ionic charges in the (100) atomic chain, the new configuration proved to be very instable, the ions returned to their initial positions and no metastable defect could arise (at least at the energies $E_R < 200$ eV). On the contrary, in NaI a defect pair bi-vacancy + crowdion appears in the process.

Although only ionic crystals and metals have been considered the applied method may be also used for MD simulations of defects formation in other crystals. The described here ILMs with the frequency above the phonon spectrum may exist also in crystals with covalent forces, e.g. in Si [13].

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