VNU Journal of Science, Mathematics - Physics 24 (2008) 223-230

Calculation of dispersion relation and real atomic vibration of fcc crystals containing dopant atom using effective potential

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Received 16 June 2008

Abstract. A new procedure for calculation and analysis of dispersion relation and real atomic vibration of fcc crystals containing dopant atom has been developed using anharmonic effective potential. Analytical expressions for dispersion relation separated by acoustic and optical branches; forbidden zone; effective force constant; Debye frequency and temperature; amplitude and phase of real vibration of atomic chain containing dopant atom have been derived. They contain Morse potential parameters characterizing vibration of each pair of atoms. Numerical calculations have been carried out for Cu doped by Ni or by Al. The results agree well with fundamental properties of these quantities and with experimental values extracted from measured Morse parameters.

1. Introduction

The real atomic vibration is oft concerned with presence of dopant atom, and study of thermodynamic properties of substances in this case is an interesting topic [1,2]. The atomic vibration is always governed by certain interatomic potentials [1,2]. Morse potential has been calculated [1,3], but for crystals the single pair interatomic potential is not enough for description of the atomic vibration [4], and the effective interatomic potential model has been developed to consider the local force constant in XAFS (X-ray Absorption Fine Structure) investigations [3,5-8]. For a two-atomic system the XAFS cumulants can be expressed as a function of a force constant of the one-dimensional bare interaction potential [4,9]. For more detailed description of thermodynamic effects of the substances it is necessary to calculate the dispersion relation between frequency and wave number, the amplitude and phase of the real atomic vibration.

The purpose of this work is to develop a new procedure for calculation and analysis of the dispersion relation determining acoustic and optic branches, the forbidden zone between them, the amplitude and phase of the real atomic vibration of fcc crystals containing a dopant atom. Our development is the derivations of analytical expressions for these quantities where the anharmonic effective potential has been applied to calculation of the effective force constant. This effective potential is constructed by including the influence of immediate atomic neighbors and the Morse

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potential parameters characterizing interaction of each pair of atoms. Numerical calculations have been carried out for Cu doped by Ni or by Al. The results agree well with fundamental properties of these quantities and with experimental values extracted from measured Morse parameters [10].

2. Formalism

2.1. Anharmonic effective potential and effective force constant

The anharmonic effective potential for the pure materials [3, 5-8] is now generalized to the case with a dopant atom according to which the effective interaction potential of the system consisting of a dopant (D) and the other host (H) atoms is given by

$$V_{eff}(x) \cong \frac{1}{2}k_{eff}^{HD}x^2 + k_3x^3 + \cdots = V_{HD}(x) + \sum_{j\neq i} V_{HD}\left(\frac{\mu}{M_i}x\hat{\mathbf{R}}_{12}.\hat{\mathbf{R}}_{ij}\right)$$

$$= V_{HD}(x) + V_{HD}(-\kappa x) + 4V_{HD}\left(\kappa\frac{x}{2}\right) + 4V_{HD}\left(-\kappa\frac{x}{2}\right) + 4V_{HH}\left(\frac{1}{2}.\frac{x}{2}\right) + 4V_{HH}\left(-\frac{1}{2}.\frac{x}{2}\right) + V_{HH}\left(-\frac{1}{2}x\right), \quad (1)$$

$$\mu = \frac{M_D M_H}{M_D + M_H}, \quad \kappa = \frac{M_H}{M_D + M_H}. \quad (2)$$

Here x is deviation between the instantaneous bond length r and its equilibrium value r_o, k_{eff} is effective force constant, and k_3 the cubic parameter giving an asymmetry in the pair distribution function, $\hat{\mathbf{R}}$ is bond unit vector. This model is here generalized to oscillation of a pair of atoms with masses M_D and M_H (e.g., dopant and host atom) in a given system. Their oscillation is influenced by the immediate neighbors given by the 2nd term in the right side of the second of Eq. (1), where the sum i is over the central atom ($i=1$) and the correlated one ($i=2$), and the sum j is over all their nearest neighbors, excluding the central and the correlated atom. The latter contributions are described by the term $V_{HD}(x)$. The third equality is for fcc crystals.

For weak anharmonicity the Morse potential for doping case is expanded to the 3rd order

$$V_{HD}(x) = D_{HD}\left(-1 + \alpha_{HD}^2x^2 - \alpha_{HD}^3x^3 + \cdots\right), \quad (3)$$

where its parameters have been obtained by averaging those of the pure materials, and they are given by

$$D_{HD} = \frac{D_D + D_H}{2}, \quad \alpha_{HD}^2 = \frac{D_D\alpha_D^2 + D_H\alpha_H^2}{D_D + D_H}, \quad \alpha_{HD}^3 = \frac{D_D\alpha_D^3 + D_H\alpha_H^3}{D_D + D_H}. \quad (4)$$

Substituting these Morse parameters in to Eq. (1) and taking into account the atomic distribution of fcc crystal we obtain the effective force constant

$$k_{eff}^{HD} = 2\left[(1+3\kappa^2)D_{HD}\alpha_{HD}^2 + \frac{3}{4}D_H\alpha_H^2\right], \quad (5)$$

which governs the vibration process between the host (H) and dopant (D) atoms.

In the case if dopant is taken from the material, i. e., there is only vibration between host atoms, Eq. (5) will change into the one for the pure material

$$k_{eff} = 5D\alpha^2, \quad (6)$$

obtained previously in [3, 5-8].

2.2. Dispersion relation

Supposed that the host (H) atom with mass M_H is located at the point on a distance of a lattice constant *a* far from the dopant (D) atom with mass M_D, and both they are in the lattice cell *n*. The same distributions for H and D atoms are in the left $(n-2)$ and in the right $(n+2)$ lattice cells. In this case the moving equations for H and D atoms are given by

$$\begin{aligned} M_H \ddot{u}_{H,n} &= -k_{eff}^{HD}\left(2u_{H,n} - u_{D,n} - u_{D,n-2}\right), \\ M_D \ddot{u}_{D,n} &= -k_{eff}^{HD}\left(2u_{D,n} - u_{H,n} - u_{H,n+2}\right). \end{aligned} \tag{7}$$

Here the thermal displacement functions of H and D atoms are as follows

$$u_{H,n} = U_H e^{i\omega t},\ u_{H,n+2} = U_H e^{i(\omega t + 2qa)},\ u_{D,n} = U_D e^{i\omega t},\ u_{D,n-2} = U_D e^{i(\omega t - 2qa)}, \tag{8}$$

q is wave number, and the effective force constant k_{eff}^{HD} has the form of Eq. (5).

Substituting Eqs. (8) into Eqs. (7) and solving their characteristic equation we obtain solution as analytical expression for the dispersion relation between frequency and wave number

$$\omega_{\pm}^2 = k_{eff}^{HD}\left[\frac{1}{\mu} \pm \sqrt{\frac{1}{\mu^2} - \frac{4\sin^2(qa)}{M_H M_D}}\right],\quad \mu = \frac{M_H M_D}{M_H + M_D}, \tag{9}$$

which creates the acoustic (ω_-) and optic (ω_+) branches for vibration between H and D atoms.

At $q = 0$ we obtain acoustic frequency $\omega_- = 0$ and optic frequency $\omega_+ = \max$ which is itself the Debye frequency. Therefore the correlated Debye frequency and temperature are given by

$$\omega_D = \sqrt{2k_{eff}^{HD}/\mu},\quad \theta_D = \hbar\omega_D / k_B, \tag{10}$$

where k_B is Boltzmann constant.

At $q = \pm\pi/2a$ we obtain the boundary values and their difference as forbidden zone

$$\begin{aligned} (\omega_-)_{\max} &= \sqrt{2k_{eff}^{HD}/M_H}, \qquad (\omega_+)_{\min} = \sqrt{2k_{eff}^{HD}/M_D}, \\ \Delta\omega_{\pm} &= (\omega_+)_{\min} - (\omega_-)_{\max} = \sqrt{2k_{eff}^{HD}}\left(\frac{1}{\sqrt{M_D}} - \frac{1}{\sqrt{M_H}}\right), \end{aligned} \tag{11}$$

so that, at this bound we obtain the following interesting results:

a) $M_H > M_D \rightarrow \Delta\omega_{\pm} > 0$: In the lattice there is no vibration corresponding to frequencies in this zone. That means, at the bound of the 1st Brillouin zone there is a forbidden zone, where the wave with these frequencies can not be propagated and strongly absorbed.

b) $M_H = M_D \rightarrow \Delta\omega_{\pm} = 0$: The acoustic branch joins the optic one.

c) $M_H < M_D \rightarrow \Delta\omega_{\pm} < 0$: The acoustic branch overlaps the optic one.

In practice the b) and c) results are usely not real so that the forbidden zone is very important.

2.3. Real lattice vibration in presence of a dopant atom

Further we consider the atomic chain consisting of H atoms with mass M_H located on the distance of a lattice constant *a* from one another, but the central atom is replaced by a dopant with mass $M_D = M_H(1-\varepsilon)$, where $\varepsilon = 1 - M_D/M_H$ so that $\varepsilon > 0$ for $M_H > M_D$ and $\varepsilon < 0$ for $M_H < M_D$.

We denote the orders of atoms by integer number $n = 0, \pm 1, \pm 2, ..., \pm l, ...$, where (+) for H atom located on the right and (-) for those in the left of the dopant atom located at $n = 0$. In this case the system of moving equations is given by

$$\begin{aligned}
&M_H \ddot{u}_{-1} = k_{eff}^{HD}(u_{-1} - u_0) - k_{eff}(u_{-1} - u_{-2}),\\
&M_D \ddot{u}_0 = -k_{eff}^{HD}(2u_0 - u_1 - u_{-1}),\\
&M_H \ddot{u}_1 = -k_{eff}^{HD}(u_1 - u_0) - k_{eff}(u_1 - u_2),\\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\\
&M_H \ddot{u}_l = -k_{eff}(2u_l - u_{l-1} - u_{l+1}).
\end{aligned} \tag{12}$$

Using the atomic displacement functions u_n and $\omega_{\max}$ of H atom

$$u_n = U_n \exp(i\omega t), \quad \omega_{\max}^2 = 4k_{eff} / M_H , \tag{13}$$

from Eqs. (12) we obtain

$$u_1 + u_{-1} + \left[\frac{4\omega^2 k_{eff}}{\omega_{\max}^2 k_{eff}^{HD}}(1-\varepsilon) - 2\right] u_0 = 0 , \tag{14}$$

$$u_{\pm 2} + u_0 + \left[\frac{4\omega^2 k_{eff}}{\omega_{\max}^2 k_{eff}^{HD}} - \frac{\mathrm{k_{eff}}}{\mathrm{k_{eff}^{HD}}} - 1\right] u_{\pm 1} = 0 , \tag{15}$$

$$u_{l+1} + u_{l-1} + \left[\frac{4\omega^2}{\omega_{\max}^2} - 2\right] u_l = 0 , \quad (l \neq 0, \pm 1) , \tag{16}$$

where k$_{eff}$ has the form of Eq. (6).

The homogeneous differential equation Eq. (16) has the following characteristic equation

$$\lambda^{l+1} + \left[\frac{4\omega^2}{\omega_{\max}^2} - 2\right] \lambda^l + \lambda^{l-1} = 0 . \tag{17}$$

Dividing both sides of this equation by λ^{l-1} we obtain

$$\lambda^2 + \left[\frac{4\omega^2}{\omega_{\max}^2} - 2\right] \lambda + 1 = 0 , \tag{18}$$

which provides the following solution $\lambda_{1,2} = \left(1 - \frac{2\omega^2}{\omega_{\max}^2}\right) \pm \frac{2\omega}{\omega_{\max}^2} \sqrt{\omega^2 - \omega_{\max}^2}$. (19)

Now we separate the results in two cases based on the vibrating frequencies:

1) $\omega < \omega_{\max}$ (acoustic branch):

In this case $\lambda_{1,2}$ is complex and the general solution of Eq. (16) is given by

$$u_l = c_1 \cos \varphi.l + c_2 \sin \varphi.l , \tag{20}$$

$$\varphi = artg\left[\left(\frac{4\omega^2}{\omega_{\max}^2} - \frac{4\omega^4}{\omega_{\max}^4}\right)^{1/2} / \left(1 - \frac{2\omega^2}{\omega_{\max}^2}\right)\right] . \tag{21}$$

This solution can be symmetric and asymmetric. The asymmetric function is neglected because $u_0 = 0$. We use only the symmetric function $u_l = u_{-l} = c_1 \cos\varphi.l$. Substituting dispersion relation for the pure material [1]

$$\omega = \omega_{\max}\left|\sin\frac{qa}{2}\right| \tag{22}$$

into Eq. (21) we obtain $\varphi = qa$, so that $u_l = \cos(qa|l| + \delta)$. (23)

Substituting Eq. (23) into Eq. (14) with taking into account of Eq. (22) we obtain the phase shift

$$\delta = artg\left[\left(\frac{k_{eff}}{k_{eff}^{HD}} - \varepsilon\frac{k_{eff}}{k_{eff}^{HD}} - 1\right) tg\frac{qa}{2}\right], \tag{24}$$

which depends on the effective force constants and ε. Hence, the lattice defect leads to a phase shift of the lattice vibration. But in the case of small ε and $k_{eff} / k_{eff}^{HD} \approx 1$, this δ is very small.

2) $\alpha > \alpha_{\max}$ (optic branch):

In this case Eq. (16) also has characteristic equation Eq. (18) with solution Eq. (19), but in this case $\lambda_{1,2}$ is not complex so that Eq. (16) has solution in the form

$$u_l = c_1\lambda^l + c_2\lambda^{-l}, \quad |\lambda| < 1. \tag{25}$$

By further analysis we obtain

$$u_l = c_1\lambda^l \text{ for } l > 0 \;;\quad u_l = c_2\lambda^{-l} \text{ for } l < 0, \tag{26}$$

from the boundary condition ($l \to \pm\infty$), and

$$c_1 = c_2 = c \to u_0 = c, \tag{27}$$

from the symmetry of displacement functions.

Substituting Eqs. (26, 27) into Eq. (14) we obtain

$$2\lambda + \frac{4\omega^2 k_{eff}}{\omega_{\max}^2 k_{eff}^{HD}}(1-\varepsilon) - 2 = 0. \tag{28}$$

From Eq. (18) the frequency is resulted as

$$\omega^2 = -\frac{(\lambda-1)^2}{4\lambda}\omega_{\max}^2. \tag{29}$$

Substituting Eq. (29) into Eq. (28) we obtain

$$(\lambda-1)\left[2 - \frac{(\lambda-1)(1-\varepsilon)k_{eff}}{\lambda k_{eff}^{HD}}\right] = 0. \tag{30}$$

Since $\lambda \neq 1$, from Eq. (30) the parameter λ is given by

$$\lambda = \frac{(\varepsilon-1)k_{eff}}{(\varepsilon-1)k_{eff} + 2k_{eff}^{HD}}. \tag{31}$$

Substituting Eq. (31) into Eq. (26) or Eq. (18) we obtain

$$u_l = u_0(-1)^l \left\{ \frac{(1-\varepsilon)k_{eff}}{(\varepsilon-1)k_{eff} + 2k_{eff}^{HD}} \right\}^{|l|}, \; c = u_0, \tag{32}$$

or into Eq. (29) it is resulted as $\omega^2 = \dfrac{\omega_{\max}^2 \left(k_{eff}^{HD}\right)^2}{\{[(\varepsilon-1)k_{eff} + 2k_{eff}^{HD}]k_{eff}(1-\varepsilon)\}}$, (33)

Here the displacement function u_l and frequency ω depend on the effective force constants and on the mass relation between the host (M_H) and the dopant (M_D) atoms. Moreover, Eq. (33) leads to the following limiting cases

$$\lim_{k_{eff}^{HD} \to k_{eff}} \omega^2 = \frac{\omega_{\max}^2}{1-\varepsilon^2}, \quad \lim_{M_D \to M_H} \omega^2 = \frac{\omega_{\max}^2 \left(k_{eff}^{HD}\right)^2}{k_{eff}(2k_{eff}^{HD} - k_{eff})}, \tag{34}$$

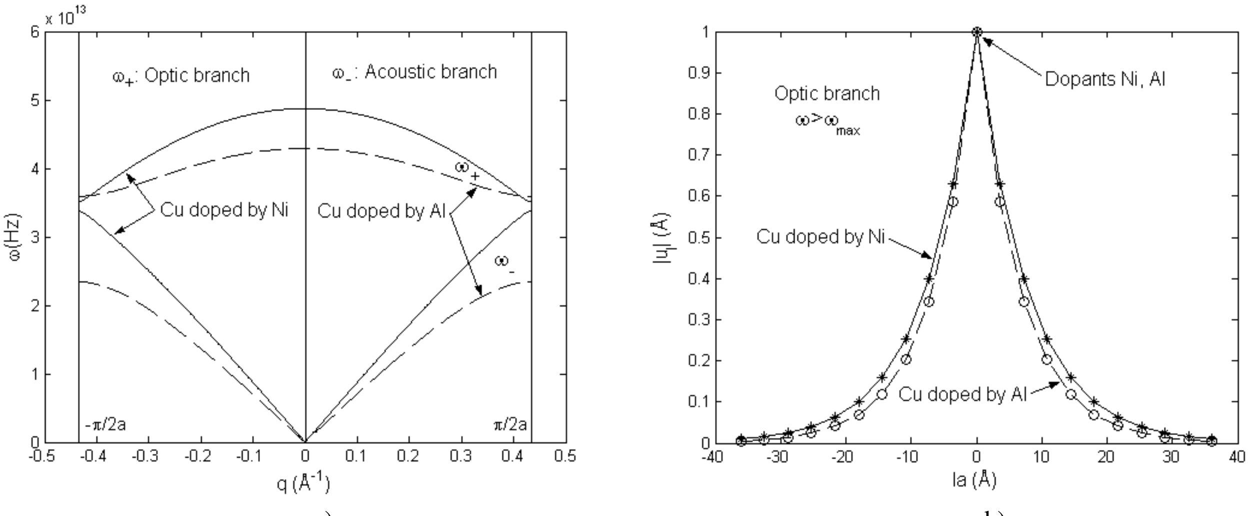
where the first case depends on ε and the second one on the force constants k_{eff}, k_{eff}^{HD}.

3. Numerical results and discussions

Now we apply the above derived expressions to numerical calculations for Cu doped by Ni or by Al atom. Their Morse potential parameters have been calculated using those of the pure materials calculated by the procedure presented in [3, 11]. The calculated values of Morse potential parameters D_{HD}, α_{HD}, effective force constant k_{eff}^{HD}, the size of forbidden zone $\Delta\omega_{\pm}$, correlated Debye frequency ω_D^{HD} and temperature θ_D^{HD} are presented in Table 1 for Cu doped by Ni or by Al. They are found to be in good agreement with experimental values extracted from the measured Morse parameters [7] for Cu doped by Ni. The forbidden zone at the bound of the 1st Brillouin zone written in Table 1 is from $3.377\times10^{13}\,Hz$ to $3.513\times10^{13}\,Hz$ for Cu doped by Ni, and from $2.341\times10^{13}\,Hz$ to $3.593\times10^{13}\,Hz$ for Cu doped by Al. Fig. 1a illustrates the calculated dispersion relation separating the acoustic and optic branches, forbidden zones for Cu doped by Ni or by Al. Here the mass of dopant Ni is close to the one of Cu (host), then the forbidden zone is small, but the mass of dopant Al is more different from the one of Cu (host), then the forbidden zone is larger. Fig. 1b shows the calculated absolute magnitudes of the vibrational function of Cu atoms for Cu doped by Ni or by Al atom in the optic branch ($\omega > \omega_{\max}$). Here the vibrations of dopants Ni and Al are localized at $l = 0$, and the mass of dopant atom Al is smaller than the one of Cu, then the amplitude changes of the atomic vibration of Cu are smaller than the one for Cu doped by Ni. Fig. 2a shows the calculated atomic vibration $u_2(l=2)$ of Cu and its phase shift for Cu doped by Ni or by Al atom. The vibrations of dopants Ni and Al are localized at $q = 0$. Here we consider the phase shift for the acoustic branch ($\omega < \omega_{\max}$), and the mass difference between Al and Cu is larger than the one between Ni and Cu, then their phase shift is larger. Fig. 2b shows the calculated amplitude changes of vibration of Cu atoms in the acoustic branch for Cu doped by Ni. Here the vibration of dopant Ni is localized at $l = 0$. All the above obtained numerical results show that they reflect the main important properties of the considered quantities in fundamental theories and in experiment [1, 2].

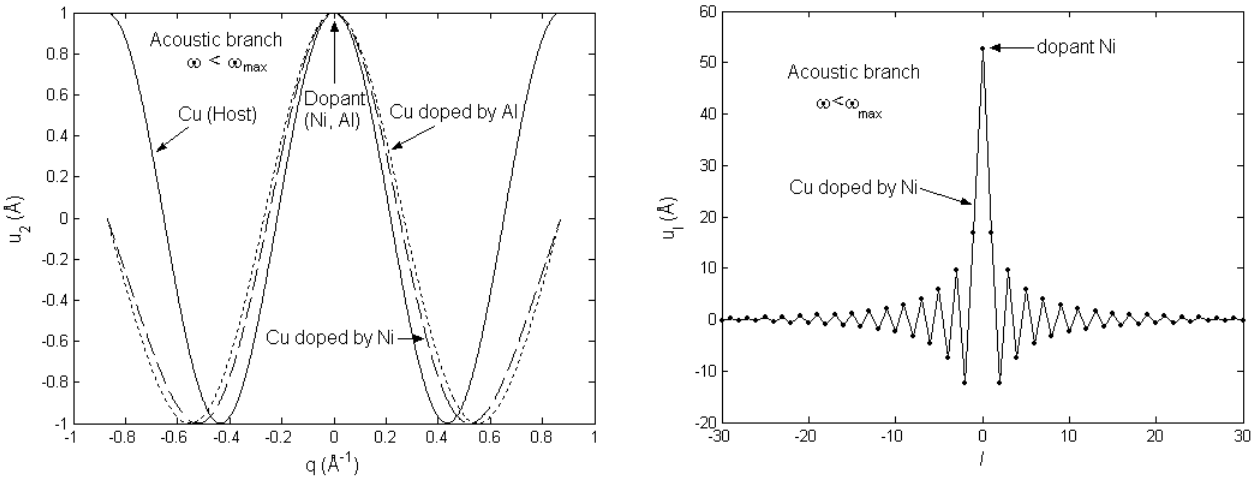
Table 1. Calculated values of D_{HD} , α_{HD} , k_{eff}^{HD} , $\Delta\omega_{\pm}$, ω_D^{HD} , θ_D^{HD} for Cu doped by Ni or by Al

Bond	D_{HD} (eV)	α_{HD} (Å^{-1})	k_{eff}^{HD} (N/m)	$\Delta\omega_{\pm}$ ($\times 10^{13} Hz$)	ω_D^{HD} ($\times 10^{13} Hz$)	θ_D^{HD} (K)
Cu-Ni, present	0.38	1.39	60.51	0.137	4.87	372.22
Cu-Ni, exp [7]	0.37	1.38	57.05	0.133	4.73	361.42
Cu-Al, present	0.31	1.28	29.10	1.252	3.38	258.10



a) b)

Fig. 1. Calculated dispersion relation separating acoustic (ω_{-}) and optic (ω_{+}) branches (a) and amplitude changes of atomic vibration of Cu atoms in optic branch (b) for Cu doped by Ni or by Al.



a) b)

Fig. 2. Calculated phase shift (a) and amplitude changes (b) of atomic vibration of Cu atoms in acoustic branch for Cu doped by Ni or by Al atom.

4. Conclusions

In this work a new procedure for calculation and analysis of the dispersion relation and real atomic vibration of fcc crystals containing dopant atom has been developed using the anharmonic effective potential.

Analytical expressions have been derived for determining the acoustic and optic branches, forbidden zone between them, effective force constant, Debye frequency and temperature, amplitude and phase changes of the real vibration of atomic chain containing dopant atom, as well as the localization of the dopant atomic vibration.

Numerical results for Cu doped by Ni or by Al agree well with fundamental properties of the considered quantities and with experimental values extracted from the measured Morse parameters. This demonstrates the efficiency and possibility of using anharmonic effective potentials in calculation and analysis of fundamental physical quantities.

Acknowledgments. This work is supported in part by the basic science research national program provided by the Ministry of Science and Technology No. 40.58.06 and by the special research project of VNU Hanoi.

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