Theoretical studies on phonon density of states in nonstoichiometric palladium hydrides

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Abstract. We investigate the phonon density of states in nonstoichiometric palladium hydrides PdHx, in order to clarify the contribution of lattice vibrations to superconductivity. We employ the Burger-MacLachlan model, which considers a one-dimensional triply-connected diatomic chains with randomly distributed vacancies, focusing on the <111> direction in the rock-salt lattice of PdHx. The phonon density of states is calculated by the forced oscillator method suitable for random systems. We find that phonon modes at high frequencies change from localized to collective modes with increasing x and the crossover stoichiometry is consistent with that of the appearance of superconductivity. These results support the optical phonon mechanism for superconductivity in PdHx.

1. Introduction

There has been considerable interest in palladium hydrides (PdHx) due to their potential applications such as hydrogen storage since Graham discovered that palladium (Pd) absorbs hydrogen (H) [1]. In addition, Skoskiewicz found that the system undergoes a transition to a superconducting state when the stoichiometry \( x \equiv \text{H/Pd} \approx 0.81 \) [2]. Interestingly, the superconducting transition temperature \( T_c \) increases up to 10 K as the stoichiometry \( x \) approaches 1 [3]. Thus, the system was considered a promising candidate for a high temperature superconductor before the discovery of copper oxide superconductors.

The mechanism of superconductivity in PdHx showing such relatively high \( T_c \) is believed to be the Bardeen-Cooper-Schrieffer (BCS) theory [4] with optical phonons as the glue for the electrons [5] since \( T_c \) is proportional to the associated phonon frequency \( \omega_B \) in the BCS framework given as

\[
k_B T_c = 1.13 h \omega_B \exp \left( - \frac{1}{N(0)V} \right)
\]

where \( k_B \) and \( h \) are the Boltzmann constant and the reduced Planck constant, respectively. \( N(0) \) and \( V \) are the electronic density of states at the Fermi surface and the coupling constant, respectively. However, it is not clear whether optical phonon modes formed by the collective motion of a large number of atoms exist in nonstoichiometric PdHx, which are random or inhomogeneous lattices, because randomness conventionally prevents from emerging collective atomic motion. In this paper, we study the competition between individual excitations and collective excitations in controlling the...
system’s randomness, i.e. stoichiometry and show the development of optical phonons from localized phonon modes as the stoichiometry $x$ increases.

2. The Burger-MacLachlan model for PdH$_x$

The crystal structure of palladium is a face-centered cubic (fcc) lattice. Hydrogen atoms adsorbed at surface diffuse into the crystal and end up being randomly distributed in the octahedral interstices, i.e. an interstitial site between six Pd sites in the fcc palladium lattice as shown in Fig. 1. Thus, PdH$_x$ is regarded as a disordered lattice. Here we employ the Burger-MacLachlan model [6] to calculate the phonon density of states. In their model, PdH$_x$ is modelled by a one-dimensional diatomic chain consisting of heavy atoms with mass $m_H$ and light atoms with mass $m_L$, taking only the dominant $<111>$ direction into account [6,7,8]. The schematic diagrams for the model we employ here are shown in Fig. 2. Heavy atoms and light atoms occupy odd sites and even sites, respectively. They are connected to each other in the nearest-neighbor form for heavy-light pairs with force constant $C_{HL}$ and the next-nearest-neighbor form for heavy-heavy and/or light-light pairs with force constants $C_{HH}$ and $C_{LL}$, respectively. Figure 2(a) shows a simple monatomic chain representing a pure palladium lattice ($x = 0.00$). Figure 2(b) shows a disordered random chain produced by the absorption of hydrogen atoms randomly located at interstitials at an intermediate stoichiometry. Figure 2(c) represents a triply-connected diatomic chain with fully occupied interstitial sites by hydrogens ($x = 1.00$).

![Figure 1](image1.png)

**Figure 1.** The crystal structure of PdH$_x$. Open circles and solid circles are palladium and hydrogen, respectively. The arrow from (0,0,0) atom represents the [111] direction. The crystal is modelled by one-dimensional diatomic chain taking only the dominant <111> direction.

![Figure 2](image2.png)

**Figure 2.** Schematic diagrams of the Burger-MacLachlan model that is triply-connected diatomic chains with randomly distributed vacancies. (a) Heavy atoms (depicted by open circles) occupy odd sites regularly. (b) Light atoms (solid circles) are placed randomly in the even site. (c) The triply-connected diatomic chains with the nearest neighbor and the next nearest neighbor atoms.

Here we summarize the analytical expression of the dispersion relation for $x = 1.00$, in order to check the reliability of our numerical simulation. The equations of motion for the atoms on 2$l$+1th site and 2$l$th site in the model shown in Figure 2(c) are given as
where \( \mathbf{u}_{2l+1} \) and \( \mathbf{u}_{2l} \) are the displacement of the heavy atom and the light atom on the \( 2l+1 \)th site and \( 2l \)th site, respectively. The dispersion relation for the model shown in Figure 2(c) is given as

\[
m_{H} \frac{d^2 \mathbf{u}_{2l+1}(t)}{dt^2} = -2(C_{H} + C_{HL})\mathbf{u}_{2l+1}(t) + C_{H}[\mathbf{u}_{2l+3}(t) + \mathbf{u}_{2l-1}(t)] + C_{HL}[\mathbf{u}_{2l+2}(t) + \mathbf{u}_{2l}(t)]
\]

and

\[
m_{L} \frac{d^2 \mathbf{u}_{2l}(t)}{dt^2} = -2(C_{L} + C_{HL})\mathbf{u}_{2l}(t) + C_{L}[\mathbf{u}_{2l+2}(t) + \mathbf{u}_{2l-2}(t)] + C_{HL}[\mathbf{u}_{2l+1}(t) + \mathbf{u}_{2l-1}(t)]
\]

where \( \mathbf{u}_{2l+1}(t) \) and \( \mathbf{u}_{2l}(t) \) are the displacement of the heavy atom and light atom on the \( 2l+1 \)th site and \( 2l \)th site, respectively. The dispersion relation for the model shown in Figure 2(c) is given as

\[
\omega^2(k) = \omega_0^2 \pm \omega_0^2 \left[ 1 - 8 \left( \frac{\omega_H^2 + \omega_L^2}{\omega_0^2} \right) \sin^2(ka) + \frac{\omega_H^2}{\omega_0^2} \left( \frac{\omega_H^2}{\omega_0^2} r_H + \frac{\omega_L^2}{\omega_0^2} r_L \right) \right]^{1/2},
\]

where we define \( \omega_0^2 \equiv 2(\omega_H^2 + \omega_L^2) \sin^2(ka) + \omega_0^2 \right) \omega_H^2, \omega_L^2 \equiv C_{H}/m_{H} \) and \( \omega_L^2 \equiv C_{L}/m_{L} \). We also define \( \omega_0^2 \equiv C_{HL}/\mu \) and \( \omega_0^2 \equiv C_{HL}/M \) with \( M \equiv m_{H} + m_{L} \) and \( 1/\mu \equiv 1/m_{H} + 1/m_{L} \) being the total mass of atoms and the reduced mass, respectively. The ratio of \( m_{H} \) to \( m \) and \( m_{L} \) to \( m \) are \( r_H \) and \( r_L \), respectively. The phonon density of states \( D_T(\omega) \) can be expressed as

\[
D_T(\omega) = \pm \frac{N \omega}{\pi \omega_0^2} \left[ \left( \frac{\omega_H^2}{\omega_0^2} - 2\gamma \right) (1 \pm Z) + \frac{4\sigma^2}{v^2} \left[ 1 - \frac{\omega_0^2}{\omega_0^2} - 2\gamma \right] \right] \times \left( \frac{\omega_H^2}{\omega_0^2} - 2\gamma \right) Z \left[ \left( \frac{\omega_H^2}{\omega_0^2} - 2\gamma \right) (1 \pm Z) \right]^{1/2},
\]

where

\[
y = \frac{(\omega_0^2 + \omega_H^2 r_H^2 + \omega_L^2 r_L^2)}{v^2},
\]

and

\[
Z = \left[ 1 + \frac{4\sigma^2 \omega_0^2}{v^2} \right]^{1/2} \frac{\left( \frac{2 - \omega_0^2}{\omega_H^2} \right)}{\left( \frac{2 - \omega_0^2}{\omega_0^2} \right)^2}.
\]

Here we also use \( v^2 \equiv \omega_0^2 + \omega_L^2 \) and \( 1/\sigma^2 \equiv \omega_0^2 / \omega_H^2 \). Equation (5) can be reduced to well-known expressions for monatomic and diatomic chains when \( C_{HL} = 0 \) and \( C_{H} = C_{L} = 0 \), respectively.

### 3. Forced oscillator method

In the previous section, we obtained analytical formulae for the phonon density of states in specific situations such as \( x = 0.00 \) and 1.00. However, there is no simple way to obtain similar expressions analytically at intermediate values of the stoichiometry due to randomness. Therefore, we use a numerical method for obtaining the phonon density of states.

In the numerical approach for lattice vibrations, the most essential part of the calculations is to find the eigenvalues and eigenvectors of large matrices [9]. However, it is extremely difficult to find them due to physical limitations of computers, e.g., memory resources, as the size of the matrices increases. Therefore, alternative approaches are highly desirable.

Here, we employ the forced oscillator method (FOM) introduced by Williams and Maris [10] in 1985, and later developed by Yakubo and Nakayama [11,12,13] to calculate the phonon density of states for disordered lattice vibrations. The method is based on resonance phenomena applying a random external force to each atom at rest given by

\[
F_l = F_0 \cos(\phi_l) \cos(\Omega t),
\]

where \( F_0 \) is a constant amplitude, the phase \( \phi_l \) and \( \Omega \) are a random variable with respect to the site number \( l \) and a frequency of external force, respectively. These random forces compensate the
randomness of the system by averaging over the entire system. In the FOM calculations, the phonon density of states is given by

\[ D_F(\Omega) = \frac{\langle E(\Omega, T) \rangle}{\pi T^2 N}, \]

where \( \langle E(\Omega, T) \rangle \) is the averaged total energy of the system after time \( T \) and \( N \) is the total number of atoms in the system. Thus, we can calculate the phonon density of states only from the time-averaged energy for the forced vibrations without finding all eigenvalues and eigenvectors. Thus, the FOM is suitable for analyzing the disordered system dealing with in the present study.

4. Numerical results

4.1. Parameters

In Fig. 3, we present the phonon density of states at various values of the stoichiometry \( x \) calculated from the FOM. In the FOM calculations, the number of lattice points was set to \( N = 100,000 \). The force constants that we used are \( C_{HL}/C_H = 0.18 \) and \( C_L/C_H = 0.16 \) \( (C_H = 373.069 \times 10^{-3} \text{ kg/s}^2, C_L = 59.691 \times 10^{-3} \text{ kg/s}^2 \text{ and } C_{HL} = 67.152 \times 10^{-3} \text{ kg/s}^2) \) estimated from the result of Rowe et al. [14] based on neutron diffraction experiments. The mass ratio is \( m_L/m_H = 1/106 \) \( (m_H = 177.421 \times 10^{-27} \text{ kg} \text{ and } m_L = 1.674 \times 10^{-27} \text{ kg}) \). The FOM solutions are represented as circles with a dashed line, while theoretical solutions are depicted by solid lines shown in both Fig. 3 (a) for a monatomic chain \( (x = 0.00) \) and (f) for a diatomic chain \( (x = 1.00) \). From those, one can easily identify acoustic phonon modes at lower frequencies and optical phonon modes at higher frequencies. In addition, there is no appreciable difference between the results of the analytical and FOM calculations. This demonstrates the reliability of the FOM calculation.

![Figure 3](image)

**Figure 3.** The phonon density of states at various values of the stoichiometry \( x \). The circles and dashed line are FOM solutions, while the solid lines are the analytical solutions given in Eq. (5). The FOM solutions in Fig. (a) and (f) are in good agreement with the analytical solutions.
4.2. Numerical results
Let us observe the phonon spectra at intermediate stoichiometric ratios. At \( x = 0.20 \) (Fig. 3 (b)), some peaks appear at high frequencies. These are due to localized lattice vibrations regarded as excitations of individual light atoms. The number of peaks increases with increasing \( x \), with these peaks all lying in the frequency range corresponding to optical phonons (see Fig. 3 (c) to (e)). Figure 4 shows the density of states enlarged the optical phonon part at various \( x \) values ranging from 0.60 to 1.00. A large number of localized lattice vibrations are shifted to a collective motion of a large number of atoms called optical phonon modes. These results imply that the optical phonon modes are developed from localized lattice vibrations as \( x \) increases.

![Figure 4](image-url)

**Figure 4.** Enlarged drawings of the optical phonon part in the phonon density of states at various values of stoichiometry \( x \) ranging from 0.60 to 1.00. A large number of localized lattice vibrations are shifted to a collective motion of a large number of atoms with increasing \( x \). 

4.3. Correlations
Now let us consider the crossover from localized lattice vibrations to optical phonon modes as a function of \( x \). To evaluate how similar localized lattice vibrations \( D_F(\omega, x) \) to optical phonon modes \( D_F(\omega) \) at stoichiometry \( x \) are, we introduce the correlation \( C(x) \) defined as

\[
C(x) = \frac{\sum_\omega D_F(\omega)D_F(\omega, x)}{\sum_\omega D_F^2(\omega)}.
\]  

(10)

There is no correlation if \( C(x) = 0 \), while perfect correlation if \( C(x) = 1 \). Figure 5 shows the correlation as a function of \( x \). The circles are the calculated correlations and the solid line is a fitting function \( f(x) \) that is a 6th-order polynomial. The correlation first gradually increases at smaller \( x \) values. On the other hand, the correlation rapidly increases at large \( x \) values. To see this dependence more clearly, we take the derivative of correlations \( dC(x)/dx \) in Fig. 6. This figure shows that \( dC(x)/dx \) has two different positive slopes in the low stoichiometry range (dot line) and the high stoichiometry range (dash-dotted line). The lower slope indicates the growth of localized phonon modes, while the higher slope implies that of extended optical phonon modes. These distinct slopes crossover at around \( x = 0.80 \) which is roughly consistent with the stoichiometry for the appearance of superconductivity in PdH\(_x\).

![Figure 5](image-url)

**Figure 5.** The correlation function defined by Eq. (10) as a function of stoichiometry \( x \). The solid line is the 6th order fitting function \( f(x) \).
Figure 6. The derivative of correlations as a function of stoichiometry \( x \). There are two different positive slopes, one for the localized phonon range (dotted line) and the other for the optical phonon range (dash-dotted line).

5. Concluding remarks
The mechanism of superconductivity in nonstoichiometric PdH\(_x\) has been hypothesized to be optical phonon-mediated BCS theory. However, it is not clear how the disordered hydrogen atoms produce the optical phonon modes. Therefore, we have investigated the phonon density of states in the triply-connected diatomic chains with randomly distributed vacancies. The correlation \( C(x) \) clearly unveiled two types of lattice dynamics in nonstoichiometric palladium hydrides. This suggests that the localized phonon modes transform into the optical phonon modes. In addition, we found that the crossover stoichiometry is roughly consistent with that of the appearance of superconductivity. This supports the existing optical phonon mechanisms for palladium hydrides. We will extend the one-dimensional Burger-MacLachlan model to three-dimensional cases to confirm these results in more realistic situations.

Acknowledgements
We would like to thank K Yakubo for his FOM programs and technical inputs. We are also grateful to S Tamura, S Ashhab, S Ishizaka and T Inagaki for helpful discussions and suggestions.

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