

Precise solution for H-point oscillation: Mo, Na, and Fe

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 L453

(<http://iopscience.iop.org/0953-8984/14/25/103>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 18/05/2010 at 12:07

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Precise solution for H-point oscillation: Mo, Na, and Fe

Y Wang¹, R Ahuja¹, O Eriksson¹, B Johansson^{1,2} and G Grimvall³

¹ Condensed Matter Theory Group, Department of Physics, Uppsala University, Box 530, S-751 21, Uppsala, Sweden

² Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology, S-100 44, Stockholm, Sweden

³ Theory of Materials, Royal Institute of Technology, KTH-SCFAB, S-106 91, Stockholm, Sweden

Received 1 May 2002, in final form 22 May 2002

Published 14 June 2002

Online at stacks.iop.org/JPhysCM/14/L453

Abstract

In the existing theory of lattice dynamics, the central roles are played by the harmonic and the quasi-harmonic approximations. In this letter, we try to derive an accurate solution for the one-dimensional oscillator, exemplified by the H-point phonon in body-centred cubic metals. This problem is formulated such that it takes the form of a one-dimensional periodic system. Mo, Na, and Fe have been chosen as prototypes and we have examined the changes of the phonon energies with temperature and pressure. We are able to reproduce, for the first time, the anomalous temperature dependence of the H-point phonon energy for Mo.

Detailed knowledge of the lattice vibrations in solids is enormously important [1–6] for understanding the quantum mechanical forces that bind the atoms together and describing temperature-driven phase transitions using the free energy method. Although several attempts have been made along these lines there are, as we shall describe below, important questions covering intrinsic anharmonicity that have not yet been answered.

For a solid at low temperature, it is a well established practice to approximate the potential energy of the system by a parabola. Considerable progress [7–9] has been achieved and in general very good agreement with experiments has been obtained, except for some cases where anomalous behaviour of phonon frequencies has been observed.

When the temperature is raised or the potential energy deviates from the harmonic approximation, the anharmonicity becomes important [10, 11]. An important distinction has to be made between the quasi-harmonic approximation (QHA) and intrinsic anharmonicity (IA). Except for the volume dependence of the force constants, QHA is in essence a harmonic approximation which only considers the second-order term in the Taylor expansion of the

potential energy. The IA, which is present at constant volume for certain substances, arises from the terms higher than second order in the Taylor expansion of the potential energy.

Theoretically, there are two ways to account for the IA. The widely adopted one is the perturbational technique (PT). However, the PT does not give an accurate solution. For example, the explanation of certain issues such as the anomalous temperature dependence [12] of the H-point phonon of Mo remains an open question. The second way is to accurately solve the vibrational Schrödinger equation. This was first accomplished by Ho *et al* [13], studying the vibrations of hydrogen isotopes in NbH, and later done by Elsässer *et al* [14] for weakly anharmonic vibrations of H in bcc NbH and for strongly anharmonic vibrations of H in fcc PdH.

In this letter, we extend the approach of Ho *et al* [13] to the case of the H-point phonon for a bcc crystal. By viewing the H-point lattice mode as a one-dimensional periodic system of atoms, we do not adopt the concept of phonons from the harmonic approximation but relate the phonon energies to a statistical average of the calculated energy eigenvalue spectra. As will be seen, our results are most encouraging in that both the measured temperature and pressure dependences of the H-point phonon are well reproduced in the framework of state-of-the-art, solid-state quantum mechanical calculations.

In the bcc metal, the so-called H-point oscillation is formed by two equivalent atoms from the primitive simple cubic unit cell moving in opposite directions [15]. In principle, this is a three-dimensional question. However, the much heavier atomic mass of Mo compared to that of H makes the true three-dimensional solution of the vibrational Schrödinger equation and the 0 K electronic total-energy calculations tremendously time-consuming. The compromise is to adopt the one-dimensional approximation. This approach is supported by the fact that the inelastic neutron measurement is usually performed in a specifically polarized direction. More specifically, we study the H-point oscillation by considering that the atom in the body-centre position in the bcc unit cell is uniformly distorted towards the face-centre position ((001) polarization). Figure 1 displays the calculated curve of the total energy of the H-point oscillation as a function of the atomic displacement away from the body-centre position. Notice that the ‘moving atom’ can also cross the face-centre position towards the next body-centre position. This forms a straightforward physical picture of an atom in a one-dimensional periodic potential field. We can naturally solve such a system, using an approach analogous to a one-dimensional electronic energy band theory [16].

Let us detail the solution for the system illustrated in figure 1. Let $V(x)$ be the calculated total energy as a function of the distance x of the ‘moving atom’ away from the body-centre position with $V(x) = V(x + a)$, where a represents the lattice constant of the bcc unit cell; then the energy eigenvalue spectrum $\{\epsilon_0, \epsilon_1, \dots\}$ of the system can be derived by solving the following secular equation for an atom in a periodic potential field:

$$\left[\frac{\hbar^2 G^2}{2\mu} - \epsilon \right] C(G) + \sum_{G'} U(G - G') C(G') = 0, \quad (1)$$

where \hbar is the Planck constant divided by 2π , μ is the effective mass of a two-atom system, $U(G)$ is the coefficient of Fourier transformation of $V(x)$, and $C(G)$ is the coefficient of the linear combination of the ‘one-atom’ wavefunction with the plane-wave basis $\exp(iGx)$.

In order to calculate the 0 K total energy, the full-potential linearized augmented plane-wave (LAPW) [17] method within the generalized gradient approximation (GGA) [18] is employed. We use constant muffin-tin radii (R_{mt}) of 2.0, 1.75, and 2.0 au for Mo, Fe, and Na, respectively. The plane-wave cut-off K_{cut} is determined from $R_{mt} K_{cut} = 9.0, 9.0, \text{ and } 8.0$ for Mo, Fe, and Na, respectively. For the reciprocal-space integrations we use 1000 k -points in the full zone. The 0 K total energy is calculated with a lattice displacement step of $0.02 a$

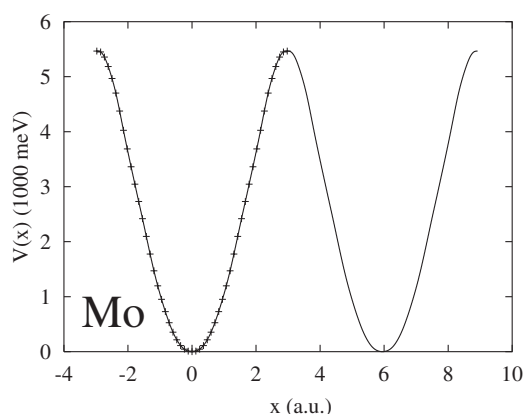


Figure 1. The potential energy, $V(x)$, as a function of the lattice displacement, x , of the body-centre atom in the case of the H-point oscillatory mode for Mo. The plus signs indicate the points calculated using the full-potential LAPW method. The solid curve is from the cubic spline interpolation.

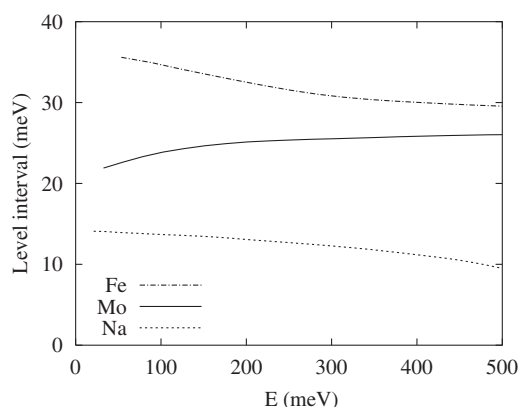


Figure 2. The calculated energy space (ESA) between the adjacent energy levels as a function of the energy eigenvalue (E) for Mo, Na, and Fe at their lattice constants under normal conditions.

corresponding to the H-point oscillation with $\langle 001 \rangle$ polarization. Then a denser set of points corresponding to a lattice displacement step of $0.001 a$ are derived by cubic spline interpolation, and used as the input to the fast Fourier transformation to produce $U(G)$ in equation (1). The convergence was tested by varying the number of plane waves needed to solve equation (1). We found that 500 ($|a/2\pi G_{\max}| = 250$) plane waves were more than enough to give fully convergent results within the energy range of interest.

As regards the results, let us first focus on the energy eigenvalue spectra as the essential aspect in understanding the IA versus the QHA. Figure 2 shows the calculated energy space (ESA) between the adjacent energy levels as functions of the energy eigenvalue for Mo, Na, and Fe at their lattice constants under normal conditions.

The first important result of the present approach is that, contrary to what was found from the QHA, at a fixed volume, the ESA is no longer a constant. In fact, the results for Mo, Na, and Fe show three different behaviours, which we now describe.

Molybdenum (Mo)

The IA is particularly evident for Mo where the ESA increases sharply with increasing energy for the first few energy levels, then becomes almost constant, and then decreases (not shown in figure 2). This is very relevant for the understanding of the anomalous behaviour in Mo.

Sodium (Na)

Na represents the ‘normal case’, where the ESA decreases slowly with increasing energy.

Iron (Fe)

Fe represents the ‘strong-softening case’, where the ESA decreases sharply with increasing energy for the first few energy levels, then becomes almost constant.

We turn to the interesting question regarding the temperature dependence of the H-point phonon energy. Since we derive the energy eigenvalue spectra directly from the potential energy by means of equation (1) without using the harmonic approximation, we have lost the very concept of the phonon [19]. Therefore we must deduce an equivalent concept from the energy eigenvalue spectra.

The intuitional picture is that if the calculated ESA becomes smaller (larger) with increasing energy, the phonon energy will soften (stiffen). From the energy eigenvalue spectra, we can define two physical quantities. The first is the total thermal energy E :

$$E = \frac{1}{Z} \sum_n [\epsilon_n - \epsilon_0] \exp[-\beta \epsilon_n], \quad (2)$$

where ϵ_0 is energy eigenvalue of the ground state (zero-point energy), $\beta = 1/(k_B T)$, T is the temperature, k_B is Boltzmann’s constant, and Z is the ‘partition function’ in the form

$$Z = \sum_n \exp[-\beta \epsilon_n]. \quad (3)$$

The second is the number of ‘effective exciters’ N :

$$N = \frac{1}{Z} \sum_n n \exp[-\beta \epsilon_n]. \quad (4)$$

Here we suggest two ways to define the ‘effective phonon’ from E and N .

- (i) Considering the statistically averaged excitation energy, we define the ‘averaged’ phonon as

$$P_a = \frac{E}{N}. \quad (5)$$

- (ii) Considering the differential ratio of the thermal energy E against the number of ‘effective exciters’ N , we define the ‘instantaneous’ phonon as

$$P_i = \left(\frac{\partial E}{\partial N} \right)_V = \frac{(\partial E / \partial \beta)_V}{(\partial N / \partial \beta)_V}. \quad (6)$$

Note that in the case of a harmonic system where $\{\epsilon_0, \epsilon_1, \dots\}$ are equally spaced, both equations (5) and (6) give the harmonic phonon energy exactly.

In figure 3 we have plotted the calculated temperature dependences of the phonon energy at normal pressure calculated using both equations (5) and (6), using the experimental curves of the lattice constant versus temperature [20, 21], for Mo, Na, and Fe, together with the measured data [12, 22–26] with error bars if available. We find that equation (6) does indeed give better

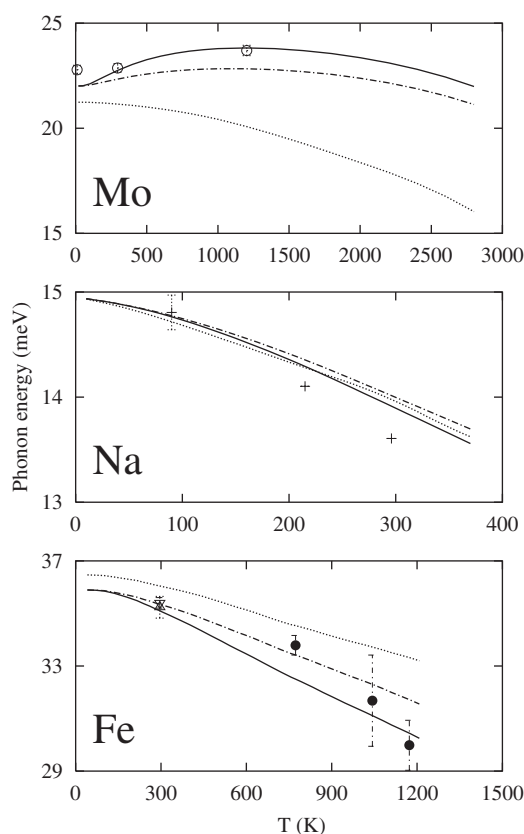


Figure 3. The H-point phonon energies against temperature at normal pressure for Mo, Na, and Fe. The solid curves are the results calculated using equation (6) and the dot-dashed curves those calculated using equation (5). The dotted curves are the results calculated using the harmonic approximation. For the measured data, the circles are from [12], the plus signs are from [22, 23], the upward-pointing triangle is from [24], the downward-pointing triangle is from [25], and the solid circles are from [26].

results compared with equation (5). The agreement between the calculations and experiments is fairly good if we consider the uncertainties of the experiments and the accuracies of the current 0 K first-principles method. (One should bear in mind that 0.3 THz corresponds to 1.2 meV.)

Again, the most interesting case is the H-point phonon of Mo, the main issue being how to explain its behaviour with temperature. In the temperature range between 10 and 1200 K, the measurements [12] show an upward rise in the phonon energy with temperature. This has attracted a lot of attention [3–6, 12, 15], but no *ab initio* calculations are known to reproduce this anomaly. Many researchers have tried to attribute the anomaly to a many-body renormalization of the electronic structure near the Fermi level leading to a breakdown of the frozen-phonon description. In a few cases, researchers have considered that it might be due to the inaccurate treatment in the existing method of lattice dynamics—the QHA. In the present calculation, the temperature dependence of the H-point phonon of Mo is reproduced for the first time. In particular, when the temperature is raised from 0 to 1200 K, our calculation shows that the phonon energy increases, rather than decreases. The additional finding from the present study

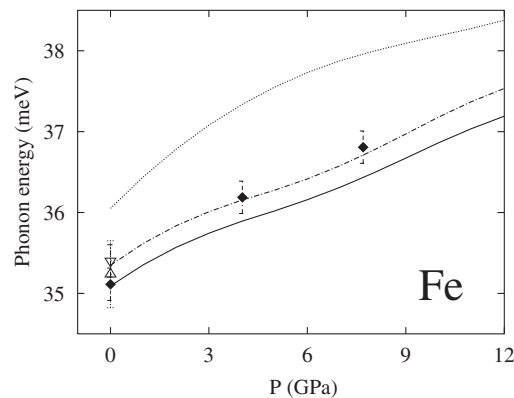


Figure 4. The H-point phonon energies against pressure at room temperature for Fe. The solid curve shows the results calculated using equation (6) and the dot-dashed curve those calculated using equation (5). The dotted curve is the result calculated using the harmonic approximation. The upward-pointing triangle is from [24], the downward-pointing triangle is from [25], and the solid diamonds are from [27].

is that if the temperature is raised further above 1200 K, the temperature dependence of the H-point phonon energy of Mo is normal, i.e. it starts to decrease as it does for the other normal metals. This theoretical prediction awaits future experiments for verification.

The one remaining doubt is that the anomalous phonon behaviour of Mo might be due to the experimental uncertainties. This is not the case. In fact, the error bar of the experimental data obtained by Zarestky *et al* [12] in the temperature range 10–1200 K is about 0.2 meV, which is quite a lot less than the phonon energy increase of 0.88 meV.

For comparison, in figure 3, we also plotted the calculated phonon energies using the conventional harmonic approximation (dotted curve). Under the harmonic approximation, the temperature dependence of the phonon energy can only emerge through volume change. As mentioned by Singh and Krakauer [15], in the case of Mo, the calculated phonon energies can only decrease with increasing temperature which is at variance with experimental findings [12]. We note that at 1200 K, the harmonic approximation produces a phonon energy of 20.1 meV, which is 15% lower than the experimental value of 23.7 meV.

The last test of the present approach is to study the pressure dependence of the phonon energy. In a very recent letter, Klotz and Braden [27] reported experiments on the phonon dispersion of bcc iron up to 10 GPa. Our calculated results for the H-point phonon of Fe are compared with their data in figure 4. We found that our calculated results agree well the experimental data.

In summary, we have extended the approach of Ho *et al* [13] to the case of the H-point phonon for a bcc crystal. It is of physical interest that we try to shed light on the accurate solution for the lattice oscillation without using the concept of harmonic approximation or QHA. The most important consequence of our calculation is that the long-standing question of the temperature dependence of the H-point phonon for Mo has been answered. We believe that the present approach will not be limited to the H-point oscillation. It is quite general as long as the potential is periodic—such as in the phonon softening of $L(2/3, 2/3, 2/3)$ in the bcc- ω phase transition [1, 28]. We also assume that the present approach can be applied simply to the case where the second-order derivative of the potential energy is negative [10].

This work was supported by Swedish Foundation for Strategic Research (SSF), Swedish Natural Science Research Council (NFR), and Göran Gustafsson Foundation.

References

- [1] Ho K M, Fu C L, Harmon N, Weber W and Hamann D R 1982 *Phys. Rev. Lett.* **49** 673
- [2] Fu C L, Ho K M, Harmon N and Liu S H 1983 *Phys. Rev. B* **28** 2957
- [3] Ho K M, Fu C L and Harmon N 1984 *Phys. Rev. B* **29** 1575
- [4] Ye Y Y, Ho K M, Chen Y and Harmon N 1991 *J. Phys.: Condens. Matter* **3** 9629
- [5] Haas H, Wang C Z, Föhnle M, Elsässer C and Ho K M 1998 *Phys. Rev. B* **57** 1461
- [6] Haas H, Wang C Z, Ho K M, Föhnle M and Elsässer C 1999 *J. Phys.: Condens. Matter* **11** 5455
- [7] Debernardi A, Alouani M and Dreyssé H 2001 *Phys. Rev. B* **63** 064305
- [8] Frank W, Elsässer C and Föhnle M 1995 *Phys. Rev. Lett.* **74** 1791
- [9] Caciuc V, Postnikov A V and Borstel G 2000 *Phys. Rev.* **61** 8806
- [10] Willaime F and Massobrio C 1991 *Phys. Rev. B* **43** 11 653
- [11] Debernardi A 2000 *Solid State Commun.* **113** 1
- [12] Zarestky J, Stassis C, Harmon B N, Ho K M and Fu C L 1983 *Phys. Rev. B* **28** 697
- [13] Ho K M, Tao H J and Zhu X Y 1984 *Phys. Rev. Lett.* **53** 1586
Tao H J, Ho K M and Zhu X Y 1986 *Phys. Rev. B* **34** 8394
- [14] Elsässer C, Ho K M, Chan C T and Föhnle M 1991 *Phys. Rev. B* **44** 10 377
Elsässer C, Ho K M, Chan C T and Föhnle M 1992 *J. Phys.: Condens. Matter* **4** 5207
- [15] Singh D and Krakauer H 1991 *Phys. Rev. B* **43** 1441
- [16] Kittel C 1996 *Solid State Physics* (New York: Wiley)
- [17] Blaha P, Schwarz K and Luitz J 1997 *WIEN97* Vienna University of Technology
This is an improved and updated Unix version of the original copyrighted WIEN code, which was published by Blaha P, Schwarz K, Sorantin P and Trickey S B 1990 *Comput. Phys. Commun.* **59** 399
- [18] Perdew J P, Burke S and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
- [19] Guillermet A F and Grimvall G 1991 *Phys. Rev. B* **44** 4332
- [20] Kennedy G C and Keeler R N 1972 *American Institute of Physics Handbook* 3rd edn, ed D E Gray (New York: McGraw-Hill) pp 4–39
- [21] Touloukian Y S, Kirby R K, Taylor R E and Desai P D 1975 *Thermophysical Properties of Matter* vol 12 (New York: Plenum)
- [22] Woods A D B, Brockhouse B N, March R H, Stewart A T and Bowers R 1962 *Phys. Rev.* **128** 1112
- [23] Glyde H R and Taylor R 1972 *Phys. Rev. B* **5** 1206
- [24] Brockhouse B N, Abou-Helal H E and Hallman E D 1967 *Solid State Commun.* **5** 211
- [25] Minkiewicz V J, Shirane G and Nathans R 1967 *Phys. Rev.* **162** 528
- [26] Neuhaus J, Petry W and Krimmel A 1997 *Physica B* **234** 897
- [27] Klotz S and Braden M 2000 *Phys. Rev. Lett.* **85** 3209
- [28] Petry W, Heiming A, Trampenau J, Alba M and Vogl G 1989 *Physica B* **156–7** 56
Güthoff F, Petry W, Stassis C, Heiming A, Hennion B, Herzig C and Trampenau J 1993 *Phys. Rev. B* **47** 2563
Petry W, Trampenau J and Herzig C 1993 *Phys. Rev. B* **48** 881