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Vibrational properties and thermochemistry from first principles

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The simulation of vibrational properties and finite temperature effects based on ab initio calculation of phonons within the direct approach is discussed. The implementation of the approach within an automated computational framework is outlined, and applications in rather diverse fields are demonstrated: phonon dispersion of GaAs, Kohn anomaly in Niobium, rattling modes in thermoelectric skutterudites, reaction enthalpies and formation enthalpies of hydrides and hydrogen storage materials, phase transformations, surface reconstruction of Si(111), and adsorption of CO molecules on a Ni(001) surface.

Key words: *computations; property predictions; ab initio*

1. Introduction

For decades, ab initio calculations have been largely viewed as being restricted to 0 K, or more precisely, as being condemned to operate without any concept of temperature. Nowadays, this major constraint has been lifted, and routine methods to evaluate vibrational properties and temperature dependent thermodynamic functions have become available, at least within the harmonic approximation. In this paper, the basic concepts of the so-called direct approach [1, 2] to vibrational properties are summarized and a number of applications in rather diverse fields are discussed. In a routine manner, free energies, vibrational enthalpies and entropies of solid compounds can be evaluated, thus enabling the study of the thermochemistry of chemical reactions as well as phase stability from ab initio theory. As will be shown, in particular for hydrogen containing compounds, neglecting zero point vibrations in many

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cases may cause qualitatively wrong answers. In addition, phonon instabilities of metastable phases may point towards possible phase transformations to other stable phases. Furthermore, vibrational spectra of transition states are well suited for the study of chemical kinetics as well as transport properties, thus opening the field for simulating diffusion processes. The methodology is, however, not restricted to the solid state: vibrations of molecules and molecules on surfaces may help to analyze spectral data, and the calculation of surface phonons is well suited to confirm the stability of a suggested surface or may reveal possible reconstructions, to indicate some of the rather promising, though challenging, applications.

2. Computational approach and implementation

During the last decade two different approaches for evaluating vibrational properties of condensed, ordered systems from first principles have evolved. Density functional perturbation theory has been implemented mainly in plane wave based density functional codes to obtain force constant matrices directly from linear response expressions [3]. In contrast, in this paper, the alternative, so-called direct approach [1, 2] is discussed, that does not require specialized ab initio codes, but can operate with any first principles code able to accurately compute the forces on atoms. From the structure model of 3D translational symmetry, a suitably large supercell is constructed to ensure that the range of interaction of each atom of the structure is, to a large extent, confined inside this supercell. Within this supercell, each asymmetric atom of the structure model is displaced in three independent directions, and for each displacement, the forces on all the other atoms arising from this displacement are calculated by an ab initio method. The number of displacements, though, may be reduced by the site symmetry. From the computed data, the force constant matrices are assembled. The Fourier transformation of the force constant matrix yields the dynamical matrix defined in reciprocal space, the diagonalization of which provides the complete phonon spectra together with the polarization vectors. Sampling the phonon spectra for a large number of q vectors in the Brillouin zone provides the phonon density of states, from which thermodynamic functions and neutron scattering data are obtained.

Based on the work of Parlinski [1], the above procedure has been implemented to operate in a fully automatic fashion together with the Vienna Ab-initio Simulation Package (VASP) [4] within the MedeA scientific modeling environment [5]. The whole process is automatically executed, starting from the supercell setup, symmetry analysis, displacing atoms, farming out VASP calculations to the available computers in a distributed network, collecting and retrieving ab initio results, assembling the force constants matrix and its diagonalization, evaluation of thermodynamic functions, down to the analysis and display of results. Even though for complex systems a large number of steps and calculations are required, this implementation enables such calculations to be performed in a rather routine manner.

3. A wide range of applications

The accuracy of the methodology is demonstrated for two cases where accurate experimental data on phonon frequencies are available from neutron scattering: GaAs and Nb. Applications are given in different fields to show the possible large impact the methodology may have on the research process: rattlers in thermoelectric skutterudite compounds, formation and reaction enthalpies, bcc to hcp phase transformations, surface reconstructions and the adsorption of molecules on surfaces.

The site preference of hydrogen in aluminum is a further example discussed in the paper by Wimmer presented in this issue [6]. For conciseness, a detailed discussion of computational aspects and results has to be presented elsewhere.

3.1. Assessment of the accuracy: GaAs and Nb

The accuracy of phonon frequencies is demonstrated for the case of GaAs in Fig. 1. Rather typically, the discrepancies between measured and calculated frequencies do not exceed a few tenths of a THz (except for the LO mode at Γ that cannot be obtained). Of course, GaAs is not a challenging test case since the phonons are well-behaved. Rather the opposite case is the phonon dispersion of bcc-Nb that exhibits drastic Kohn anomalies throughout the Brillouin zone. The rather peculiar dispersion curves along the Γ–H direction obtained experimentally and by the computation are compared in Fig. 2, revealing excellent agreement even for this outstanding case.

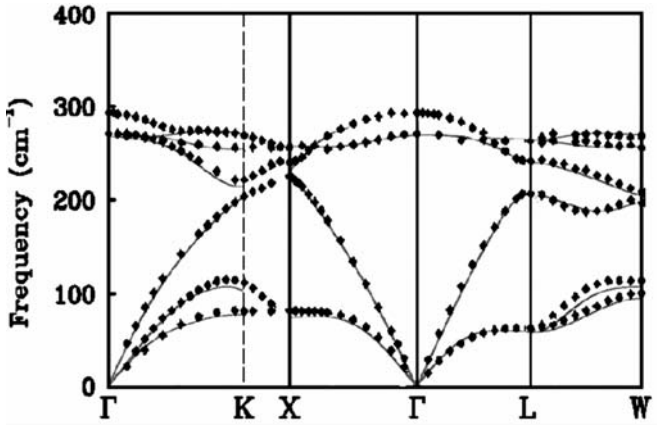

Fig. 1. Experimental phonon dispersion data (diamonds) from Ref. 7 and calculated phonon spectra from first principles (lines) for GaAs

It is noted, furthermore, that the vibrational modes of molecules are obtained with the same precision as phonon modes, provided the molecule is embedded in a suitably large cell to minimize the interaction to translational symmetry copies.

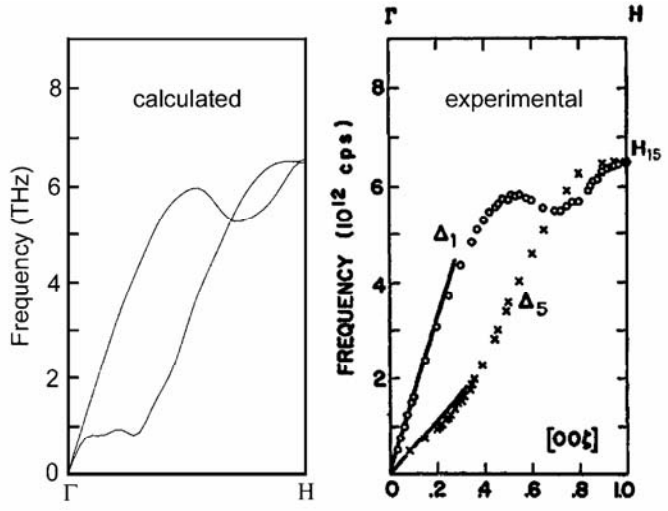

Fig. 2. The Kohn anomaly in bcc Nb along the *Γ–H* direction. Experimental phonon dispersion data from Ref. 8 and calculated phonon spectra from an elongated supercell of 45 Å in the (001) direction

3.2. Thermoelectric skutterudite materials

In recent years, renewed efforts have been undertaken to find and improve thermoelectric materials for cooling and the generation of electricity. The thermoelectric figure of merit *ZT*

$$ZT = \frac{\sigma S^2 T}{\kappa}$$

can be optimized by combining high electric conductivity σ (like a metal), high thermopower or Seebeck coefficient *S* (like a semiconductor) and low thermal conductivity κ (like ceramics or glass). Skutterudites MX_3 (M = Co, Rh, Ir, and X = P, As, Sb) are promising materials for thermoelectric applications [9]. The thermal conductivity of the antimonides could successfully be reduced by filling the voids of the structure by large and heavy atoms such as lanthanides, actinides or earth alkaline metals, thus improving considerably their figure of merit. It was speculated that the mechanism for reducing thermal conductivity might be attributed to long wavelength phonons emitted by the loosely bound filling atoms in the voids, which may couple with those phonons mainly responsible for thermal conduction. Indeed, the calculated phonon dispersion and densities of states of $LaFe_4P_{12}$ and $LaFe_4Sb_{12}$ strongly support the existence of these 'rattler modes' in the vibrational spectrum. Whereas for the phosphide the La related modes are completely separated from the others (see Fig. 3), the modes of Sb character couple strongly with the La modes.

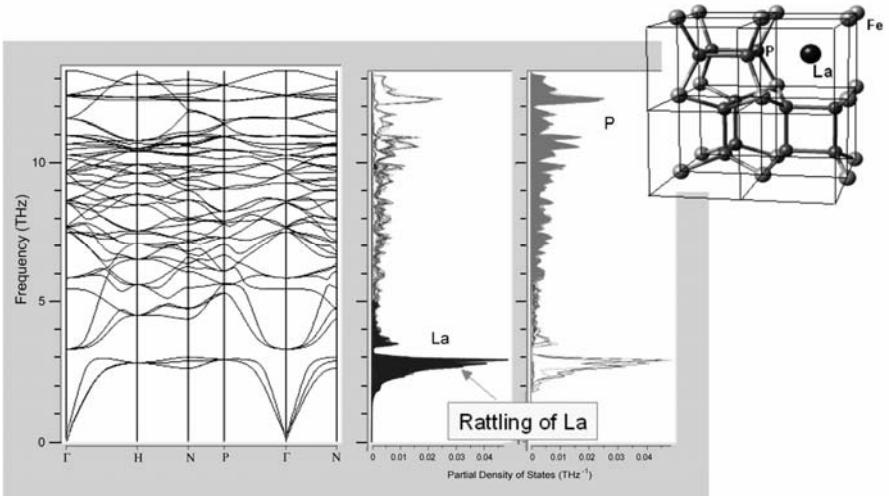

Fig. 3. Calculated phonon dispersion and phonon density of states of $LaFe_4P_{12}$. The unit cell is shown in the insert

Thermal conductivity is considered to be mainly mediated by the pnicogene (P, As, Sb) sublattice. Thus, the experimental finding that filling voids with heavy atoms is able to reduce thermal conductivity of antimonides but not of phosphides can, on the basis of the calculated phonon spectra, be understood.

3.3. Thermochemistry: enthalpies of formation and reaction enthalpies

The direct approach to vibrations is directly applicable to thermochemistry once the reactants are solid state phases or gases. The importance of vibrational contributions is emphasized by two examples in hydrogen chemistry. Table 1 provides several contributions to the reaction enthalpy of the chemical reaction of hydrogen with vanadium; the electronic part as calculated from first principles, the zero point energy, and

Table 1. Enthalpy of the reaction for the hydration of vanadium. Calculated electronic and vibrational contributions and experimental results from Ref. [10]. Energies in $kJ \cdot mol^{-1}$

Value	$2V + ½\ H_2 \rightarrow V_2H$	$V + H_2 \rightarrow VH_2$
Electronic energy (ab initio)	–40	–67
Energy including zero point vibration	–38	–45
Enthalpy at 298 K	–41	–54
Experiment	–35	–40

the temperature dependent free energy including the vibrational entropy. The small contribution of electronic enthalpy originating from exciting electrons into excited

states with increasing temperature is neglected. In fact, different vanadium hydrides may form, V_2H and VH_2. Whereas vibrational contributions to the reaction enthalpy are almost negligible for the formation of V_2H, for VH_2 the zero point energy contribution amounts to as much as 1/3 of the electronic part. In conclusion, even for quite related systems the estimation of vibrational effects is difficult and calculations are required.

Much research effort is put into the development of hydrogen storage materials as an enabling technology for future replacement of natural oil based industries. Table 2 lists the calculated results for temperature dependent heats of formation of some complex hydrides that are among the most promising candidates. Experimental data are included. For all compounds the electronic energy turns out to be quite close to experimental results. Including zero point vibrations causes considerable deviation, however, raising the temperature to the standard condition of 298 K, the good agreement is restored. These data illustrate that good agreement between the energies of formation, as calculated from first principles, and experimental data obtained at standard temperature, may often be due to the zero point energy and temperature effects cancelling out each other.

Table 2. Formation enthalpy of hydrogen storage materials. Calculated electronic and vibrational contributions compared to experimental results of Ref. [11] and references therein. Energies in $kJ \cdot mol^{-1}$

Value	$LiAlH_4$	Li_3AlH_6	LiH
Electronic energy (ab initio)	–98	–295	–83
Energy including zero point vibration	–77	–258	–77
Enthalpy at 298 K	–96	–288	–84
Experiment	–107	–300	–91

3.4. Soft modes and phase transformations

Soft modes in the phonon dispersion indicate phase transformations and may be used to explore the transformation path towards a stable phase. However, approximations or computational issues may cause unphysical complex frequencies, too, and careful studies are necessary. A rather simple example is the bcc to hcp transformation of rhenium. Whereas tungsten is stable in the bcc structure, as demonstrated by its phonon dispersion shown in Fig. 4a, the dispersion of the neighbouring element rhenium in this structure exhibits strong soft modes at the H and N point, in particular (see Fig. 4b).

Indeed, Re is known to be stable in the hcp structure. Soft phonon modes at the N point correspond to collective movements of atoms in the (110) direction without restoring forces. As illustrated in Fig. 4c, this movement leads to a bcc to hcp phase transformation path.

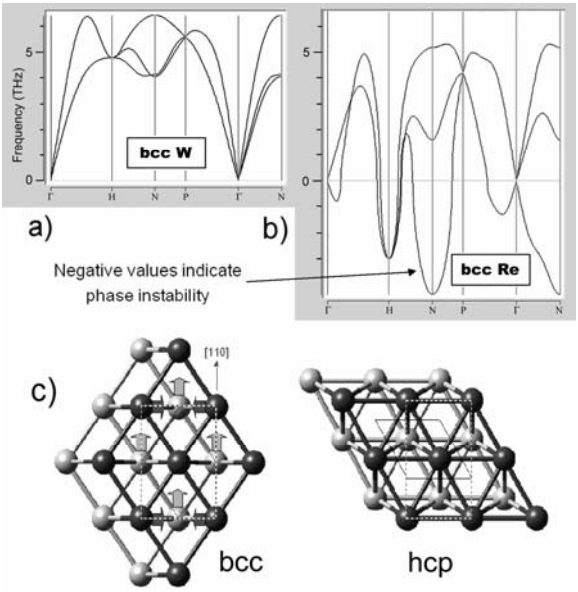

Fig. 4. Calculated phonon dispersion of bcc W (a), bcc Re (b), and bcc to hcp phase transformation path (panel c)

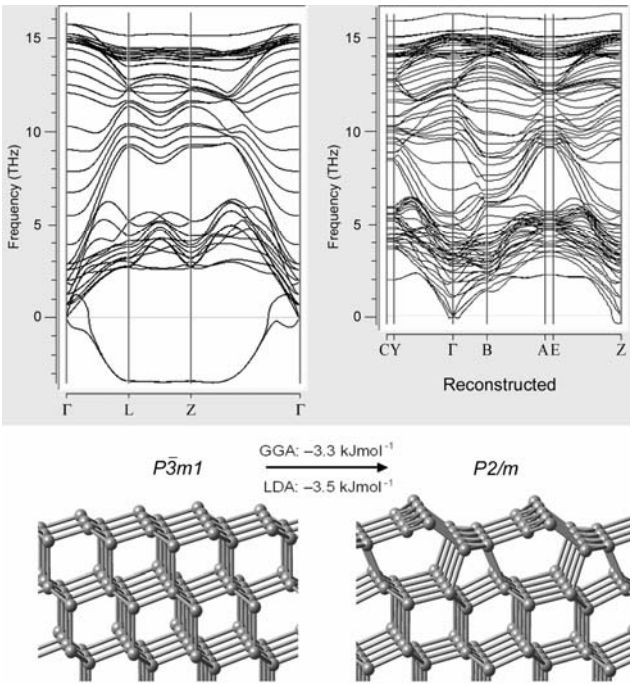

Fig. 5. Calculated phonon dispersion of unreconstructed and 2x1 reconstructed Si(111) surface. The surface structures are shown below the corresponding dispersion curves

3.5. Surface phonons and surface reconstructions

The calculation of vibrational spectra is not limited to bulk phases or molecules, because surfaces or interfaces may also be tackled by the method. As a two-dimensional analogue of the phase transformation of bulk materials, soft modes of surface phonon spectra may indicate surface reconstructions. It is well known from low-energy electron diffraction experiments (LEED) [12] that the Si(111) surface exhibits a 2×1 π-bonded chain reconstruction. The calculated phonon dispersion of slab models for the unreconstructed and 2×1 reconstructed Si(111) surfaces are shown in Fig. 5.

The unreconstructed surface is destabilized by soft phonon modes corresponding to vibrations of the surface Si atoms. On the other hand, the phonon dispersion of the reconstructed Si(111)2×1 surface slab model is mostly free of soft modes. The complex frequencies close to the Γ and Z point of the slab model's Brillouin zone are due to vibrations of the whole slab against its symmetry copy, i.e. an artifact of the slab model to surfaces.

3.6. Molecules on surfaces

Adsorption processes of molecules on surfaces are studied experimentally by measuring the change of the vibration spectra upon adsorption. In fact, shifts of frequencies may occur and are interpreted in order to gain insight into adsorption geometry and coverage. Comparison to calculated vibration frequencies for different model structures provides a valuable insight and may considerably facilitate interpretation of experimental data.

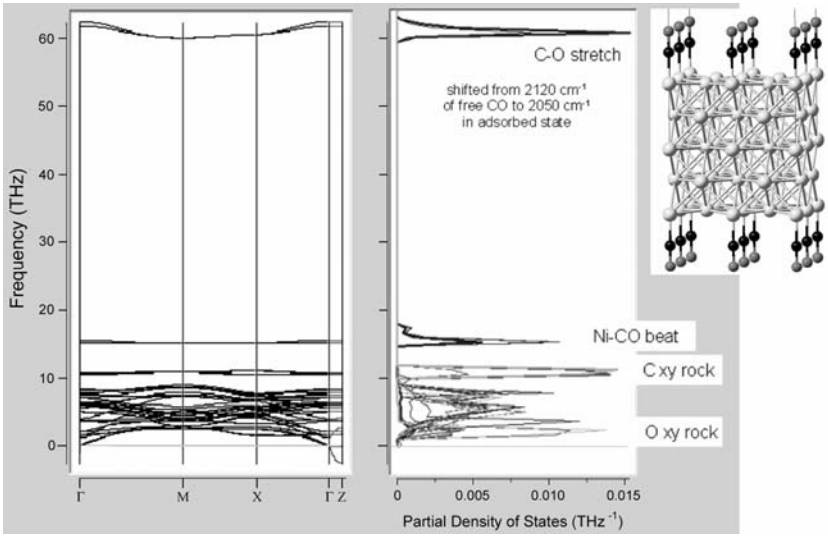

Fig. 6. Calculated phonon spectrum and density of states of the Ni(001) with (2×2) adsorbed CO molecules

In Figure 6, the phonon dispersion curves and density of states of a 5-layer slab model for the c(2×2) coverage of CO molecules on the Ni(001) surface is shown.

The highest frequency of 2050 cm^{-1} is found to correspond to the C-O stretch vibration. A reference calculation for the isolated gas phase CO molecule yields a stretch frequency of 2120 cm^{-1}. Indeed, experimental data indicate a shift of the gas phase frequency of 2140 cm^{-1} down by about 70 cm^{-1} upon adsorption [13], which is in good agreement to the calculation. Furthermore, Ni-CO beat, C *xy* rock and O *xy* rock vibration frequencies can be attributed to animating corresponding phonon modes, thus supporting interpretation of the features in experimental spectra.

4. Summary

In summary, the direct approach to lattice vibrations and its implementation in an automated computational framework is discussed, enabling computation of vibrational properties and temperature effects from first principles in a routine manner. In order to demonstrate the huge potential of the approach for industrial research, the method is applied to a wide range of problems in materials science. The examples of applications are intended to provide hints and ideas of how this methodology may enrich the scope of simulation techniques and may have a significant impact on industrial research strategies.

References

[1] PARLINSKI K., LI Z. Q., KAWAZOE Y., Phys. Rev. Lett., 78 (1997), 4063.
[2] KRESSE G., FURTHMÜLLER J., HAFNER J., Europhys. Lett., 32 (1995), 729.
[3] BARONI S., DE GIRONCOLI S., DAL CORSO A., GIANOZZI P., Rev. Modern Phys., 73 (2001), 515.
[4] KRESSE G., FURTHMÜLLER J., Phys. Rev. B, 54 (1996), 11169; Computat. Mat. Sci., 6 (1996), 15; KRESSE G., JOUBERT D., Phys. Rev. B, 59 (1999), 1758.
[5] MedeA 1.8, Materials Design, Le Mans, France (www.MaterialsDesign.com).
[6] WIMMER E., Mat. Sci.-Poland, 23 (2005), 325.
[7] STRAUCH D., DORNER B., J. Phys. Condens. Matter, 2 (1990), 1457.
[8] POWELL B. M., MARTEL P., WOODS A.D.B., Phys. Rev., 171 (1968), 727.
[9] UHER C., *Skutterudites: Prospective Novel Thermoelectrics, in Semiconductors and Semimetals*, Vol. 69, Academic Press, 2001, p. 139.
[10] WISWALL R., [in:] G. Alefeld, J. Völkl (Eds.), *Topics in Applied Physics*, Vol. 29, Springer-Verlag, Berlin, 1978, p. 201; GRIESSEN R., RESITERER T., in: L. Schlapbach (Ed.), Topics in Applied Physics, Vol. 63, Springer, Berlin, 1988, p. 218.
[11] LØVVIK O.M., OPALKA S.M., BRINKS H.W., HAUBACK B.C., Phys. Rev. B, 69 (2004), 134117.; CHASE M.W. JR., *NIST-JANAF Themochemical Tables*, Fourth Edition, J. Phys. Chem. Ref. Data, Monograph 9 (1998), 1–1951.
[12] HIMPSEL F.J., MARCUS P. M., TROMP R., BATRA I. P., COOK M. R., JONA F., LIU H., Phys. Rev. B, 30 (1984), 2257.
[13] http://www.cem.msu.edu/~cem924sg/Topic11.pdf.

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