European Science Foundation
Standing Committee for Physics and Engineering Sciences
(PESC)

ESF PESC EXPLORATORY WORKSHOP

Workshop on *ab initio* phonon calculations

SCIENTIFIC REPORT

Cracow, Poland
2–4 December 2004

Convened by: Krzysztof Parlinski

EXECUTIVE SUMMARY

The "Workshop on it ab initio phonon calculations" has been help in Cracow, Poland in the period from **2 to 4 December, 2004**. The Workshop took place in the new lecture Hall of "prof. W.Danka" in the Pedagogical University in Cracow. The participants were accommodated in the nearby Hotels Demel and Krakowiak. The 55 participants were coming from 16 countries.

The Workshop has been organized in the frame of the Ψ_k Programme on *Electronic Structure Calculations of Solids and Surfaces Network*. The organization task has been undertaken by the Department of Materials Research by Computers of the Institute of Nuclear Physics, PAN, Cracow, and the Institute of Technics of Pedagogical University, Cracow.

The Workshop has been devoted to provide the basic knowledge in the density functional theory (DFT), and the method to calculate phonons and thermodynamical properties of crystalline systems. The DFT approach allows to finds structure, electronic properties, and interatomic forces in temperatureless (T=0K) regime, while the phonons, which can be calculated within the DFT approach, define the dynamical, and thermodynamical properties at finite temperature. During the workshop tutorials the participants had a possibility to learn how to use, and what are the peculiarities of the methods and computer codes handling the above quantities.

SCIENTIFIC CONTENT

In the first day of the Workshop there were three tutorial lectures. Georg Kresse gave a review of procedures, which lead the exact calculations of the Hellmann–Feynman forces used in the phonon and molecular dynamics calculations. The necessary conditions were specified for metallic and non-metallic systems. Selection of correct pseudopotential, selection of wave vector sampling, and values of variety of switches were discussed in details. Rules and Tables to select the most relevant pseudopotential were given. Some results for nanotubes, highlighting the accuracy attainable by the VASP code, were presented.

Peter Blaha reviewed the augmented plane wave method (APW), and later modifications introduced by Slater, Andersen, Freedman, Singh and Sjöstedt. The possibilities for structural optimization and atomic force calculations were summarized. Finally, examples to calculate phonons and predicting a structural phase transition including ferroelectric Aurivillius compound, were discussed.

Krzysztof Parlinski reviewed the direct method of calculating force constants from the Hellmann–Feynman forces under confinements imposed by the system space group. The manner to select the supercell shape and size, the necessary displacements for force calculations were specified. Examples

of phonon dispersion curves and phonon density of states were shown. The above phonon data allow to derive the thermodynamical functions in harmonic approximation, and to describe the spectra and intensity of inelastic coherent and incoherent scattering of neutrons. The temperature dependences of number of quantities can be then computed within the quasiharmonic approximation, leading frequently to very good results even close to the melting temperature.

At the end of the first day of the workshop there was a tutorial in the Computer Lab, where the participants could exercise the use of the Phonon and MedeA programs, using data of Hellmann–Feynman files already computer by VASP or Wien2k programs. This time was widely used to exchange information, and learn methodological details, which routinely are not included in published articles. All participants obtained a CD with the Mini-Phonon program, which can be used to perform simple phonon calculations in combination with an *ab initio* program, and can help to illustrate phonon physics in student educational processes.

Poster session was at the same time as the Computer Lab, but posters were displayed all over the Workshop, also during the breaks, therefore, there was enough time to look at them carefully.

In the second day of the workshop three lectures demonstrated the computed phonon and thermodynamical results in several crystalline systems. Many of these results agreed very well with the experimental finding. Mark Johnson showed that inelastic incoherent neutron scattering, and infrared absorption could be well reproduced by the phonon spectra calculated with the ab initio codes. The reported systems were crystalline bithiophene, being an essential block of a conducting polymer, benzoic acid, serving as a model hydrogen-bonded system, molecular fragments of DNA and proteins. Michael Krisch reported some inelastic x-ray scattering results, a method complementary to the coherent inelastic neutron scattering. The x-ray method is well suited for disordered systems, samples only available in small quantities, and materials studied under high pressure. Particularly interesting were the phonon results measured for Pu element, and high-T_c superconductor $Nd_{1.86}Ce_{0.14}CuO_{4+\delta}$. It was shown that by x-rays the surface phonons can also be measured. Walter Wolf referred results obtained by MedeA, which combines the softwares of VASP and Phonon. The applicability of this approach was demonstrated on temperature dependence of free energies, vibrational enthalpies and entropies of solid compounds, in surface reconstruction, phase stability and phase transitions. The method allows to treat molecules on surfaces and find the energy profile essential for diffusion.

The 13 contributed talks provided further examples of applications of ab initio phonon calculations to variety of phenomena and systems. Among the others, it was shown that phonon contribute to chemical reactions, in which

solid reactants are involved. An example of experimental studies of surface phonons on Ag(111) was given. Phonons decide about structural phase transitions. There is increasing interest to analyse atomic vibrations in the disordered systems.

ASSESSMENT OF THE RESULTS, CONTRIBUTION TO THE FUTURE DIRECTION OF THE FIELD

A number of topics have been identified as important areas for future research with increasing prospective potential. Phonon will still be using to search for soft modes and identify the structural phase transitions. Phonon calculations will facilitate the analysis of vibrations in crystals, including molecular crystals, and estimate the phonon peak's intensities in the inelastic neutron and x-ray scatterings. Knowledge of phonon vibrations allows in an ab initio way to calculate the thermodynamical functions, which are important in prediction of phase transition, phase diagrams, and some chemical reactions. The mentioned approach can be applied to bulk crystal, crystals with defects, surfaces and multilayers, hence one may study surface and interface phonons.

Number of topics still need additional implementation into the computer codes. Among them is the electron-phonon coupling constant. There is a need to calculate the anharmonic contributions to phonon shift and width, which goes beyond the quasiharmonic approximation. This should allow to include anharmonic contributions to thermodynamical functions, and to compute heat conductivity. There is an interest to study atomic vibrations in disordered and amorphous systems, which can be done, for example, by averaging phonon properties over many atomic configurations, representing the disordered system. Crystals are usually studied under hydrostatic pressure. One should, however, expect new properties, and more complex phase diagrams temperature-stress components when studying the crystals under different stress components.

FINAL PROGRAM

Wednesday, December 1, 2004

17:00– 20:00	Registration
19:00–	Informal reception at Demel Hotel

Thursday, December 2, 2004

9:00 – 9:10	Opening
9:10 – 10:40	Georg Kresse *VASP: Accurate force calculations and the VASP–PAW datasets*

10:40– 11:10	Coffee break
11:10– 12:40	Peter Blaha *Electronic structure, atomic forces and structural relaxations by WIEN2k*
12:40– 14:00	Lunch at Demel Hotel
14:10– 15:40	Krzysztof Parlinski *Calculations of phonons and thermodynamical properties of crystals by PHONON*
15:40– 16:10	Coffee break
16:10– 18:10	Tutorials, Poster Session
18:45	Bus departure from Krakowiak Hotel
18:50	Bus departure from Demel Hotel
19:00–	Dinner in Modlnica

Friday, December 3, 2004

9:00 – 10:00	Mark Johnson *Phonons in molecular crystals – from ab initio calculations to neutron scattering, x-ray and infrared data*
10:00– 10:45	Michael Krisch *Inelastic x-ray scattering from phonons at the ESRF: recent results and perspectives*
10:45– 11:15	Coffee break
11:15– 12:15	Walter Wolf *Ab-initio vibrational properties and thermodynamics from an automated computational framework*
12:15– 12:35	Wilfried Wunderlich *Ab-initio calculations for development of $SrTiO_3$-based thermoelectric materials*
12:35– 14:00	Lunch at Demel Hotel
14:00– 14:20	Sathya Hanagud *First-principles equation of state for energetic intermetallic and metal-metal oxide mixtures*
14:20– 14:40	Xuezhi Z. Ke *Lattice dynamics of sodium alanate*
14:40– 15:00	C.F.J. Flipse *Experimental observation of vibrational modes on Ag(111) along Γ–M and Γ–K directions*
15:00– 15:20	Akihide Kuwabara *First-principles calculation of lattice vibration and phase transformation in ZrO_2 polymorphs*

15:20– 15:40 Paweł T. Jochym
Phase transitions in Mg_2SiO_4 and $CaCl_2$ within quasiharmonic approximation

15:40– 16:10 Coffee break

16:10– 17:20 Tutorials

17:20– 17:40 Svein Stølen
Collective ionic motion through low-energy structural entities

17:40– 18:00 H.A. van Laarhoven
Electron- and hole- vibrational coupling in oligoacene single-crystals studied by spectroscopic methods as well as first principle calculations

18:00– 18:20 Imre Bakó
Vibration of small molecules on Pd(111), Pt(111) and Rh(111) surfaces

18:20– 18:40 Elwira Wachowicz
First stages of oxidation of the Si-rich 3C–SiC(001) surface

18:40– 19:00 Jacek Piechota
First principles study of geometry of Gd: CASTEP vs. VASP

Saturday, December 4, 2004

9:00 – 9:20 Chris E. Mohn
Genetic mapping of the potential energy surface of disordered materials

9:20 – 9:40 Krzysztof D. Meisel
Ab initio study of charged polarons in semiconducting polymers

9:40 – 10:30 Coffee break

10:30– 11:30 Tutorials

11:30– 11:45 Discussion

11:45– 12:00 Closing

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STATISTICAL INFORMATION ON PARTICIPANTS

The 55 participants were coming from 16 countries: Austria (2), Czech Republic (2), Estonia (2), Finland (1), France (6), Germany (1), Hungary (1), Japan (5), The Netherlands (5), Norway (5), Poland (16), Slovakia (1), Spain (3), Sweden (3), Swiss (1), and USA (1).