Materials Science-Poland, Vol. 23, No. 2, 2005

The growing importance of computations in materials science. Current capabilities and perspectives

ERICH WIMMER*

Materials Design s.a.r.l, 44, av. F.-A. Bartholdi, 72000 Le Mans, France

Materials scientists are facing unprecedented challenges in many areas, such as energy conversion and storage, microelectronics, telecommunication, display technologies, catalysis, and structural materials. Experimental methods generate increasing amounts of data. New computational methods, high-performance computer hardware, and powerful software environments are evolving rapidly. As a result, the importance of computational materials science is growing. The following cases illustrate the current capabilities: computed thermochemical and mechanical properties of metal hydrides show trends in the heats of formation and the hydrogen-induced softening of elastic moduli; a study of the effect of impurities on the strength of a Ni grain boundary reveals hydrogen as an embrittler and boron as a strengthener; *ab initio* phonon calculations for hydrogen impurities in aluminum show a temperature-dependent site -preference; the screened-exchange approach predicts accurate energy band gaps of semiconductors; a computational screening of hydro-desulphurization catalysts points to new combinations. The major current challenges for computational materials science include more accurate total energies, unified methods to deal with multi-phase systems, e.g., solid/liquid, novel approaches to determine complex kinetic processes, and novel concepts to bridge the atomistic and the macroscopic scales.

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

1. Background

1.1. Challenges for materials science

Our societies depend more than ever on a wide range of materials with specialized properties. For example, the transition to a hydrogen economy requires the development of viable materials for hydrogen storage. The current generation of materials is inadequate and intense worldwide research efforts are directed at the discovery and development of novel materials. In fact, the search for alternative forms of energy and

*E-mail: ewimmer@materialsdesign.com.

energy conversion systems has gained an unprecedented level of urgency. At the same time, concerns about the environment and the emission of greenhouse gases makes the quest for reliable, environmentally responsible, and globally sustainable energy systems for transportation, heating, refrigeration, and lighting even more difficult. New materials play a central role in meeting these challenges.

Communication, display technologies, and data storage are other major driving forces for the development of new materials and materials processes. For example, the discovery of the giant magnetoresistance effect (i.e. the change of the electrical conductivity due to an external magnetic field) has led to major progress in the storage capacity of magnetic disks. The development of GaN-based semiconductors has a profound impact on display technologies and lighting systems. Digital cameras are revolutionizing photography. Underlying this "disruptive technology" are charged -coupled devices used as photo-sensors which replace silver halides, light-sensitive organic pigments, and time-consuming chemical processes. However, the long-term storage of digital information is by no means guaranteed and may require new materials and technologies.

As the chemical industry strives for cleaner and environmentally sustainable processes, catalysts with high reactivity, selectivity, and durability play a central role in achieving these goals. For many of these processes, the reaction mechanisms are not understood and the development of catalytic systems is pursued by tedious empirical approaches.

1.2. The role of computational approaches

During the past decades, computational materials science has made major strides in becoming a predictive discipline, impacting fundamental science as well as the development programs of industrial materials. This progress is particularly striking for *ab initio* electronic structure methods, which are the major focus of the present conference contribution. The development of novel computational methods, algorithms, and implementations in the form of computer programs is fuelled by the breathtaking progress in computer hardware and software.

There are three major reasons for computations in materials science, namely (i) to gain a deeper understanding of materials on the atomic scale, (ii) to interpret experimental data, and (iii) to predict physical and chemical properties of materials prior to experiments.

Most materials in use are not in thermodynamic equilibrium with their environment. For example, all steel constructions in contact with the atmosphere are subject to a thermodynamic driving force towards oxides (they corrode); the complex multilayer structures forming microelectronic devices have a tendency to degrade by electromigration, diffusion and precipitation of stable phases; organic materials exposed to air, sunlight, and moisture eventually degrade to molecular systems with lower chemical potentials, ending at carbon dioxide, water, and similar small molecules.

This non-equilibrium character of materials has major consequences. It links the properties of a material intimately with the processing condition. Contrary to small molecules in the gaseous or liquid phase, solid-state materials can exhibit structures on the nano- and micro-scale, which can be decisive for their macroscopic properties. For example, the grain structure of an alloy determines the fracture toughness of a material.

In fact, structural control on the nanoscale has recently aroused considerable excitement and with good reason: starting with a small number of molecular-scale building blocks, an endless number of combinations (materials) can be created, each with different properties. Examples are the many possible forms of nanotubes and nanostructured surfaces for coatings, catalysts and sensors.

In view of all these factors, one has to conclude that computational materials science is well positioned to continue its growth and importance, helping to meet the many challenges to materials science. It is also clear that the computational materials science journey has just begun and that there are vast opportunities before us, which need to be conquered. The following sections provide a brief overview of current computational methods and a selection of illustrative examples. An analysis of the current situation and a perspective on future developments will conclude this contribution.

1.3. Theoretical foundation and computational approaches

Figure 1 illustrates the hierarchy of theoretical concepts and approaches used in computational materials science. Macroscopic systems are described by continuum

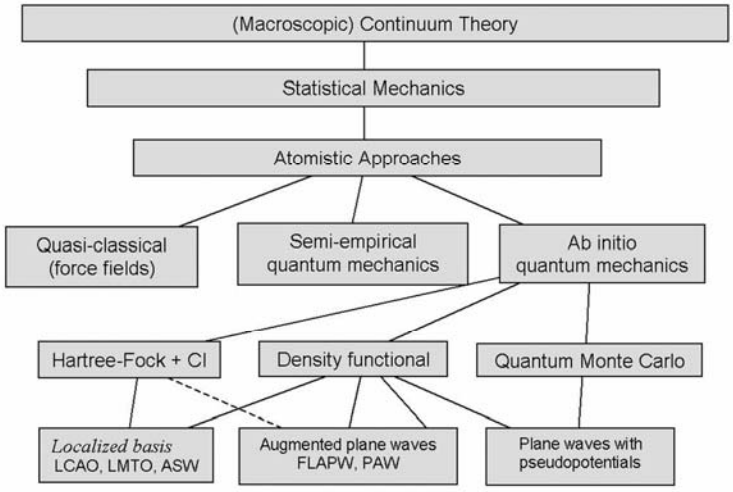

Fig. 1. Hierarchy of computational approaches for the description of molecular and solid state systems. An explanation of the abbreviations is given in the text

theory using analytical models and numerical finite element methods (FEM). In fact, FEM structural analysis and computational fluid dynamics (CFD) have become major tools in the design of cars, aircrafts, buildings, bridges, and many other engineered objects. As the resolution of FEM methods is refined, the atomistic nature of matter comes into play. It is a most intriguing question, at what scale does the atomistic aspect need to be taken into account to describe a given material and property. Is it possible to apply *ab initio* methods to systems so large that one can step directly from the *ab initio* level to continuum theory?

Statistical mechanics provides the link between assemblies of atoms and properties of macroscopic materials. The critical connection between atomistic approaches and statistical mechanics is the total energy of a system as a function of the position of the atoms in an assembly. As will be shown in the examples, the ability to compute the total energy for any type of atoms, in any arrangement, with sufficient accuracy and speed has become the cornerstone of today's computational materials science.

For convenience, the key thermodynamic and quantum mechanical definitions and formulas are given in the following section. Readers interested in the practical applications rather than the background can safely skip this theoretical part.

The Gibbs free energy is defined as

$$G = E_{\text{int}} + PV - TS \tag{1}$$

with the internal energy, E_{int}, given by

$$E_{\text{int}} = E_{\text{el}} + E_{\text{kin}} \tag{2}$$

For typical systems, the dominant term is the electronic energy, E_{el}, which includes the kinetic energy of the electrons, the electrostatic attraction between electrons and nuclei, and the repulsion between electrons and between nuclei. E_{kin} denotes the kinetic energy of moving nuclei. In the case of a solid, the kinetic energy can be written as

$$E_{\text{kin}} = E_{\text{zp}} + E_{\text{vib}} \tag{3}$$

where E_{zp} is the zero-point energy and E_{vib} the vibrational energy relative to the lowest vibrational state.

The terms P, V, and T are pressure, volume, and temperature, respectively. The entropy of a solid is given by

$$S = S_{\text{vib}} + S_{\text{config}} \tag{4}$$

with S_{vib} being the vibrational entropy and S_{config} the configurational entropy. It is now possible to compute the electronic energy as well as the zero-point energy, the vibrational internal energy, and the vibrational entropy by *ab initio* quantum mechanical methods for systems with up to approximately 100 atoms per unit cell. This capability has opened many exciting avenues, as will be illustrated in this contribution.

1.4. Atomistic approaches

On the atomic scale, three basic approaches are used, namely *ab initio* quantum mechanics, quasi-classical approaches using force fields, and semiempirical methods. By definition, *ab initio* methods are based on fundamental physical laws and constants and there are no system-specific parameters. In contrast, quasi-classical methods use interaction potentials (force fields) and parameters to describe interatomic interactions. There is a trade-off in computational efficiency and predictive capability between *ab initio* and force-field methods. A word of caution: force-field methods can be more accurate than *ab initio* methods, in particular in the description of weakly interacting systems (e.g. layers of graphite, methane molecules, and polymer chains). However, reliable and transferable force-fields for inorganic materials are difficult, or perhaps impossible, to construct. Semi-empirical methods try to strike a compromise between the rigour of electronic structure methods and the computational efficiency of parameterized force-field methods. Tight-binding theory and embedded atom or effective medium theory belongs to this class of approaches.

Ab initio methods have gained a prominent place in the description of inorganic solid-state materials while force-field methods and semi-empirical methods continue to be hampered by tedious, system-specific parameter developments.

Within *ab initio* electronic structure methods, there are currently two major many -electron theories in use, and a third approach is emerging. The two main approaches are (i) the Hartree-Fock theory with configuration interaction expansions of the many-electron wave function and (ii) density functional theory (DFT) [1] in its spin-polarized form [2] with the semi-local generalized gradient approximation (GGA) [3]. The third and emerging many-body approach is quantum Monte Carlo (QMC) method [4]. At present, DFT dominates *ab initio* computational materials science.

One of the basic tasks of quantum mechanical computations is determination of the total energy, E, of a given system as a function of the position of the atoms. This is accomplished by solving Schrödinger's equation

$$\mathbf{H}\Psi = E\Psi \tag{5}$$

where the Hamiltonian, **H**, defines the position and charge of the atomic nuclei in the system and Ψ denotes the many-electron wave function.

In DFT, the many-electron Eq. (5) is mapped onto a set of effective one-electron equations. Each of these is a one-particle Schrödinger's equation of the form

$$\boldsymbol{h}\psi_i = \varepsilon_i\psi_i \tag{6}$$

where $\boldsymbol{h}$ is an effective, one-electron Hamiltonian, ε_i are one-particle eigen values, and ψ_i are effective one-electron wave functions. Eqs. (6) are called the Kohn–Sham equations.

The total electron density, ρ, links the Kohn–Sham equations with the original many-electron Schrödinger's equation by

$$\rho = \Psi^* \Psi = \sum_i \psi_i^* \psi_i \tag{7}$$

In current electronic structure methods of molecular and solid-state systems, the one-electron wave functions, ψ_i, are expanded in a variational basis set, $\{\varphi_j\}$

$$\psi_i = \sum_j c_{ij} \varphi_j \tag{8}$$

Since the choice of the basis set is so important, specific computational methods are often named after the type of the basis set. This is the case for localized basis sets using Gaussian functions, which belong to the class of methods called linear combination of atomic orbital (LCAO) methods. It is the case for the linearized muffin-tin orbitals (LMTO) and the full-potential linearized augmented plane wave (FLAPW) methods, and it applies to pseudopotential plane wave methods. It would be beyond the scope of the present paper to review each of these methods. The interested reader is referred to review articles such as Ref. [5] and the references therein.

During recent decades, there have been heated discussions about the virtues of all-electron methods such as FLAPW versus pseudopotential methods using plane waves. During the past decade, a remarkable synthesis has been achieved between all-electron methods and pseudopotential plane wave methods by the development of the projector augmented wave (PAW) method [6] as implemented notably in the Vienna *ab initio* simulation package (VASP) [7]. This approach combines the physical aspects of all-electron methods with the elegance and computational efficiency of plane wave methods. Thus, a significant step has been achieved in advance of earlier non-local pseudopotentials and ultrasoft pseudopotentials.

2. Examples

2.1. Trends in metal hydrides

Metal hydrides are potential candidates for hydrogen storage materials. Computations are ideally suited to reveal systematic trends in the bonding geometry and the binding energy of hydrogen. Figure 2 shows such trends in the metal-hydrogen bond distance for hydrides of alkali metals, alkaline earth metals, and 3d-transition metals in cubic crystal structures.

There are three striking observations: (i) the experimental data are incomplete and computations fill in the missing data, (ii) the agreement between computed and available experimental data is excellent such that computed data can be used instead of experimental values, (iii) clear trends are visible across the transition metal series, which are not obvious using only experimental data.

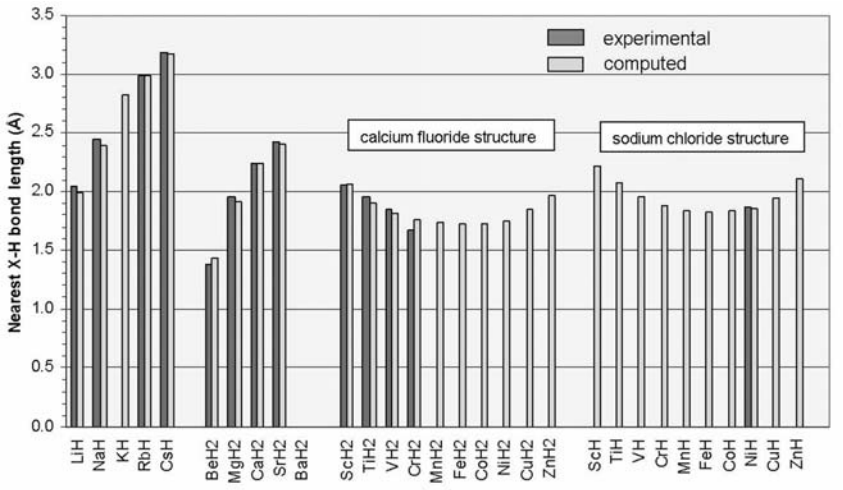

Fig. 2. Metal-hydrogen bond distances in cubic metal hydrides. Note the clear trends across the 3d-transition metal series. These trends become obvious only from the systematic computations

Figure 3 displays computed heats of formation for the reaction

$$M + ½\ H_2 \rightarrow MH \tag{9}$$

with M being a transition metal and MH is a metal hydride in the rock salt structure.

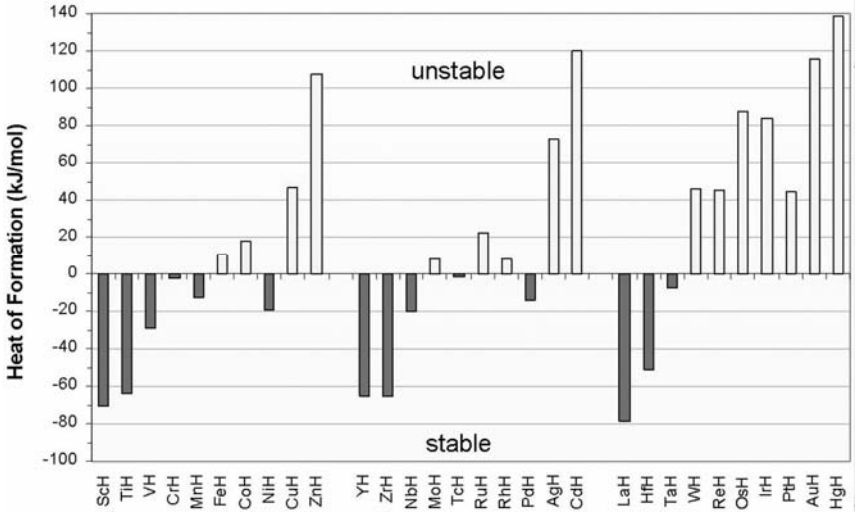

Fig. 3. Computed heats of formation of metal hydrides in the rocksalt structure

All calculations were performed on the DFT-GGA level of theory using VASP with PAW potentials. The reference state of the metal is the most stable crystalline form and gas phase molecules are used as the reference for hydrogen. In this study,

only the electronic part of the total energy is used, which is sufficient to establish the trends. The heat of formation decreases with an increasing number of *d*-electrons. Ni, Pd, and Pt are somewhat exceptional, which may be related to the ease of *s*-*d* re-hybridization.

2.2. Elastic moduli of crystalline solids

The second example demonstrates the calculation of mechanical properties on two simple systems, namely metallic nickel and nickel hydride. Nickel crystallizes with a face-centred-cubic structure. In NiH, all octahedral interstitial sites of this lattice are filled with hydrogen atoms, resulting in a rock salt structure as shown in Fig. 4.

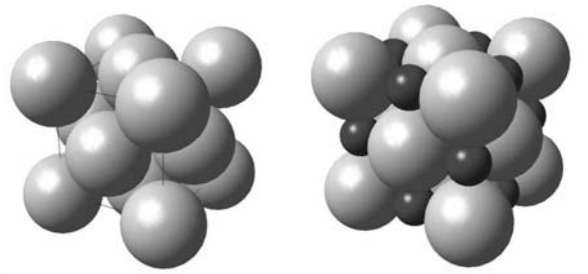

Fig. 4. Crystal structure of metallic nickel and nickel hydride

Ab initio calculations of the lattice parameter and the elastic moduli reveal an expansion of the lattice upon introduction of the hydrogen atoms. The bulk modulus remains almost unchanged, but the shear modulus and Young's modulus are reduced by more than 50%. The lowering of the shear modulus and Young's modulus imply a loss of stiffness of the material, i.e. given the same force of pulling on two opposite sides of a crystal, NiH extends more than metallic Ni.

Table 1. Computed equilibrium lattice parameters and elastic moduli for nickel and nickel hydride

Parameter	Ni	NiH
Lattice parameter (Å)	3.50	3.72
Bulk modulus (GPa)	207	198
Shear modulus (GPa)	98	41
Young's modulus (GPa)	254	116

An illustrative example of the computational accuracy of elastic constants is given by the case of aluminum nitride (Table. 2). Given the relatively large deviation between the two experimental data sets and the fact that the computed values fall overall between the experimental data, it is difficult to say, which of the three sets is actually

the most reliable. In other words, it appears that the reliability of the computed data is comparable with that of experiment.

Table 2. Experimental and computed elastic constants, C_{ij}, and the bulk modulus of hexagonal aluminum nitride. All values are given in GPa

AlN	Experiment[a]	Experiment[b]	Computation
C_{11}	345	411	375
C_{12}	125	149	130
C_{13}	120	99	100
C_{33}	395	389	347
C_{44}	118	125	113
C_{66}	110	131	122
B	202	212	195

[a]K. Tsubouchi, N. Mikoshiba, IEEE Trans. Sonics Ultrason., SU-32, 634, 1985.
[b]L. E. McNeil, M. Grimsditch, R. H. French, J. Am. Ceram., Soc. 76, 1132, 1993.

This accuracy is a most remarkable accomplishment of *ab initio* electronic structure theory. No system-specific parameters are used in the computational procedures and yet the properties of computed materials are similar to the measured data.

The computation of elastic constants for any symmetry [8] and its automation within the software environments for computational materials science [9] has now become a routine task for many systems of significant complexity. For example, this approach has been successfully applied to a mineral known as "Schorl", which belongs to the tourmaline group and has a chemical composition of $NaFe_3B_3Al_6O_{27}(OH)_3F$.

2.3. Effect of impurities on the fracture at grain boundaries

The degradation of structural engineering materials used, for example, in nuclear power reactors, is a topic of a great importance. Despite this fact, the detailed understanding of degradation processes, in particular stress corrosion cracking, is still fragmentary and there is a great need to deepen our knowledge in this field.

In this context, the effect of alloying elements, impurity atoms and nuclear transmutation products including B, Cr, H, S, P, Li have been investigated using an *ab initio* approach [10]. A Ni $\Sigma 5$ {001} twist grain boundary was chosen as a prototypical case. The modelling approach of the effect of these impurity atoms on the strength of this grain boundary is illustrated in Fig. 5.

Starting with a model of a relaxed, pure grain boundary, an impurity atom is inserted into the grain boundary. Total energy calculations are used to determine interstitial vs. substitutional impurity sites. After relaxation, the total energy of the grain boundary with the impurity is obtained. Subsequently, the system is cleaved and each of the two surfaces is relaxed. From the difference of the total energy of the surface and the grain boundary, a cleavage energy (Griffith energy) is computed.

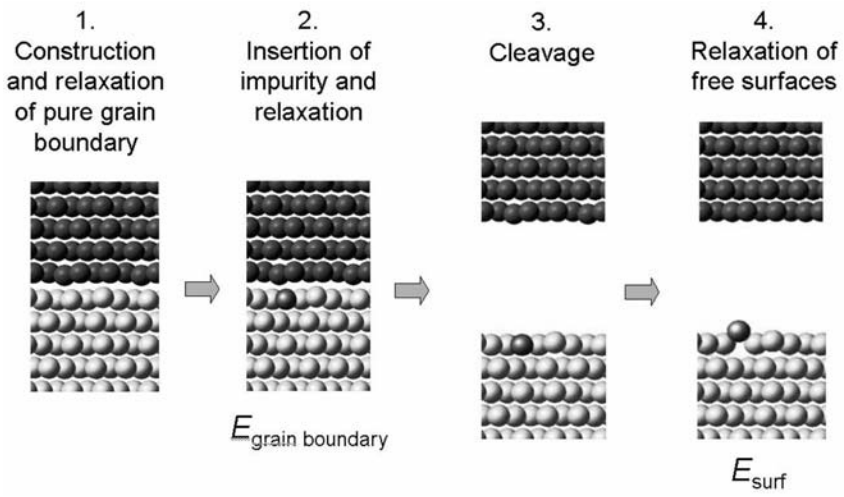

Fig. 5. Modelling of the cleavage of a grain boundary. Light and dark spheres indicate atoms of the lower and upper grain

Figure 6 illustrates the results for a series of single impurities and selected pairs of impurities.

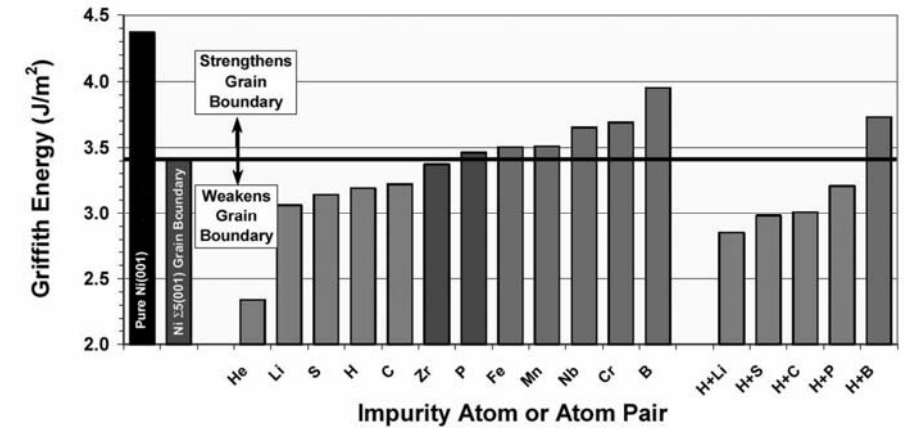

Fig. 6. Cleavage energy (Griffith energy) of bulk Ni in the (001) plane, a Ni Σ5 {001} twist grain boundary, and a series of impurity atoms and impurity pairs in this grain boundary. Note a strong weakening effect of He and Li and the strengthening of the grain boundary by boron

The cleavage energy of bulk Ni along the (001) plane is 4.4 J/m^2, which drops to 3.4 J/m^2 for a Σ5 twist grain boundary. The atoms He, Li, S, H, and C are found to weaken this grain boundary; Zr, P, Fe, and Mn are indifferent; and Nb, Cr, and especially B have a strengthening effect. Impurity pairs involving hydrogen show an additive effect on the grain boundary strength, which indicates only a weak interaction within impurity pairs.

This type of systematic, atom-by-atom comparison is a unique feature of computational modelling, since experimentally it is extremely difficult to measure the effect of each impurity atom under comparable conditions. All the calculations in this study were carried out with VASP using PAW potentials and the DFT-GGA level of theory.

2.4. Site preference of hydrogen in aluminum

The calculations discussed so far ignore any temperature dependence. Although many useful results can be obtained in this way, there are many cases, where temperature effects play a decisive role and therefore need to be included in the computational approach. An example is the behaviour of hydrogen impurities in bulk aluminum [11].

A fundamental question in the study of impurities in solids is the site preference. A conventional unit cell of an *fcc* lattice (Fig. 7) offers four octahedral and eight tetrahedral interstitial sites.

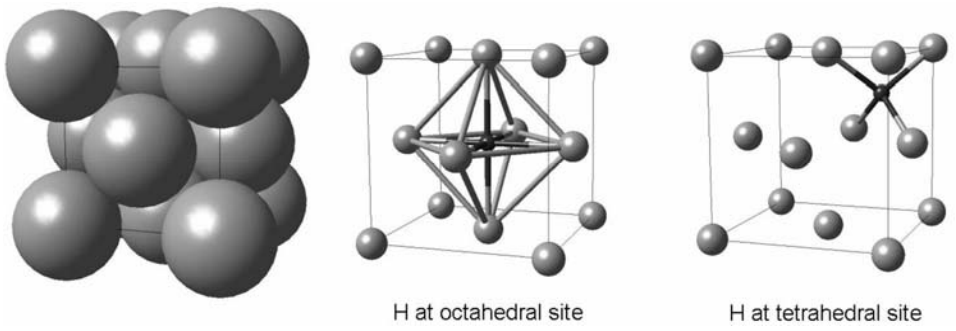

Fig. 7. Octahedral and tetrahedral interstitial sites in a face-centred cubic lattice

Using a 2×2×2 supercell containing 32 Al atoms, structural optimizations and total energy calculations show the tetrahedral site to be preferred by 12 kJ/mol compared to the octahedral site in terms of the electronic energy. However, the equilibrium of a system at finite temperature is governed by the Gibbs free energy, which contains the temperature dependence of the internal vibrational energy as well as vibrational and configurational entropy terms. In fact, low vibrational frequency modes lead to a large vibrational entropy, which lowers the Gibbs free energy at high temperature through the term $-TS$. Therefore, knowledge of the vibrational modes is a critical aspect of the system.

Using a direct phonon approach [12] and VASP, the phonon dispersion of a hydrogen impurity in aluminum was computed using a supercell of the composition $Al_{32}H$ with hydrogen in the octahedral and the tetrahedral sites. The results show (Fig. 8) that the vibrational modes associated with the hydrogen atom are shifted from 25.2 THz for H in the tetrahedral site to 10.8 THz in the octahedral site.

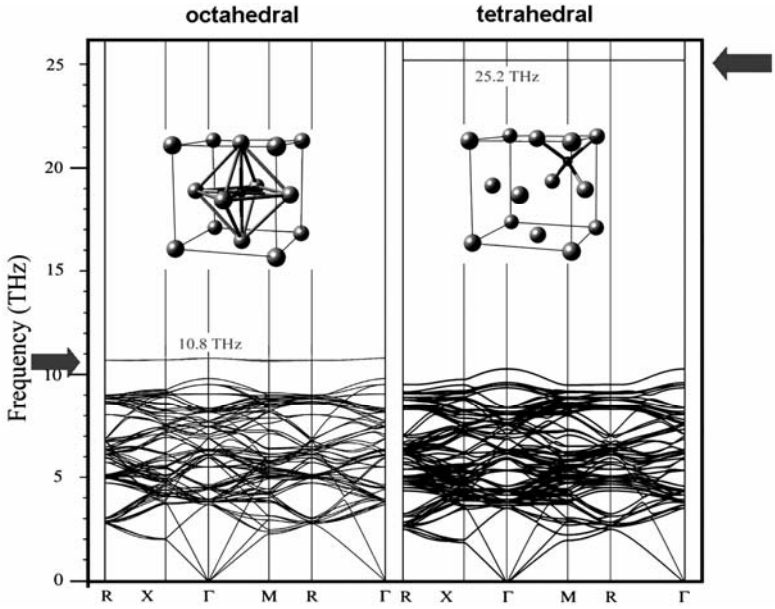

Fig. 8. Phonon dispersions of a hydrogen impurity in bulk aluminum at an octahedral and tetrahedral interstitial site. Note the dramatic shift of the H-related phonon mode (marked by arrows) between the octahedral and tetrahedral sites

As a consequence, the vibrational entropy at the octahedral site is significantly larger than at the tetrahedral site.

Figure 9 shows the difference in vibrational entropy between hydrogen in the tetrahedral and the octahedral sites.

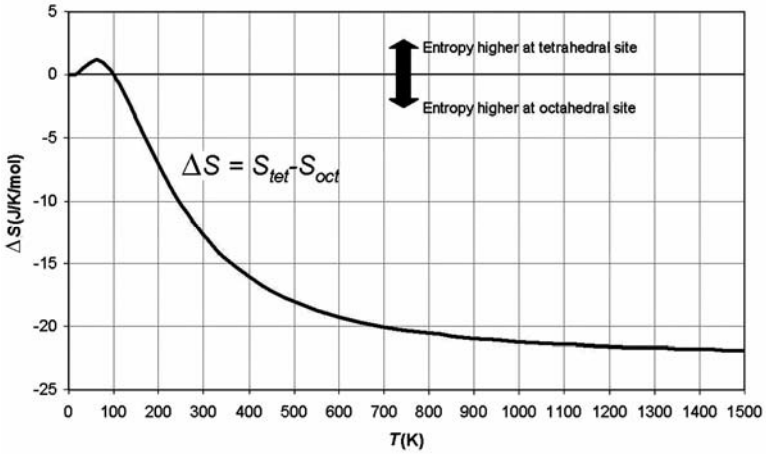

Fig. 9. Computed difference in the vibrational entropy of aluminum with a hydrogen impurity at a tetrahedral and an octahedral interstitial site. For the most part, the entropy at the octahedral site is significantly larger

As a consequence, the Gibbs free energy as a function of temperature, computed with *ab initio* theory with a phonon approach, reveals that the octahedral site is more stable for temperatures above about 400 K (Fig. 10).

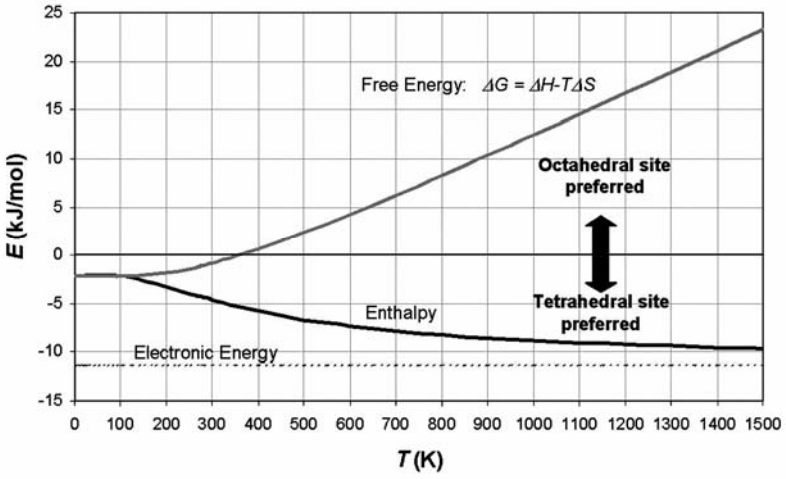

Fig. 10. Computed difference in the enthalpy and free energy of aluminum with a hydrogen impurity at a tetrahedral and an octahedral interstitial site

The results also show the importance of the zero-point energy for hydrogen. At $T = 0$, the energy difference between the tetrahedral and the octahedral sites is only about 2 kJ/mol if zero-point energy effects are included, while the electronic energy itself gives an energy difference of 12 kJ/mol in favour of the tetrahedral site.

2.5. Band gaps in semiconductors

The previous examples deal with structural, mechanical, and thermochemical properties, although in each case, the electronic wave functions and the electron densities are computed implicitly. In this example of energy band gaps, the focus is on the electronic structure involving one-electron excitation energies.

In the development of density functional theory, it was not immediately understood why the computed band gaps in semiconductors were significantly too small. Progress over the past three decades has clarified this issue and novel methods have emerged, which allow the accurate prediction of energy band gaps. One of these methods is the so-called screened-exchange approach [13], which introduces a non-local part in the effective one-electron Hamiltonian of density functional theory.

This screened-exchange approach has been implemented in the FLAPW method, leading to a remarkable accuracy in the predictions of energy band gaps for a range of semiconducting materials [14], as shown in Fig. 11. Compared with the local density approximation (LDA), the sX results are in excellent agreement with experiment, especially for narrow-band gap semiconductors such as InAs.

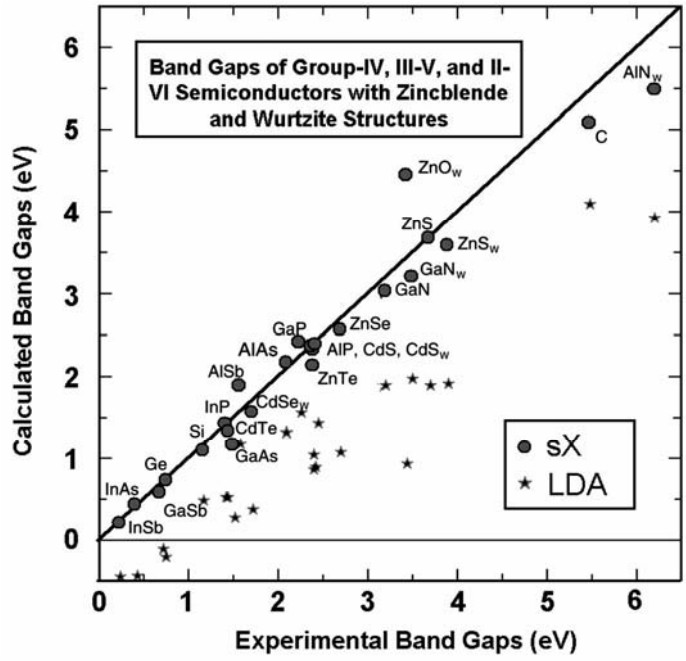

Fig. 11. Computed vs. experimental band gaps in elemental and binary semiconductors. The screened-exchange (sX) results are shown as full circes and the results from the local density approximation (LDA) are marked as stars (after Ref. 14)

The band gaps computed with the LDA are consistently too low, in some cases by as much as 50%. For narrow band gap materials, LDA predicts a "negative" band gap, i.e. the valence band and the conduction bands are predicted to overlap. Furthermore, the LDA values show a large scatter. In other words, the deviation is not due to simple scaling.

2.6. Hydrodesulphurization catalysts

The final example is taken from the field of heterogeneous catalysis. The goal of this research is the identification of the best catalytic materials, which bind selectively sulphur-containing molecules and decompose them by reactions with molecular hydrogen. This process of hydrodesulphurization plays an important role in the production of cleaner fuels (especially Diesel fuel) with reduced sulphur content.

The left side of Figure 12 shows experimentally determined catalytic activities for a list of transition metal sulphides. Unfortunately, the best materials contain rare and expensive transition metals such as ruthenium, osmium, and iridium. A large group of cheaper transition metal sulphides exhibit little activity. Intuitively, one is tempted to discard the poorly performing systems and focus the efforts on the best candidates. But where would one start?

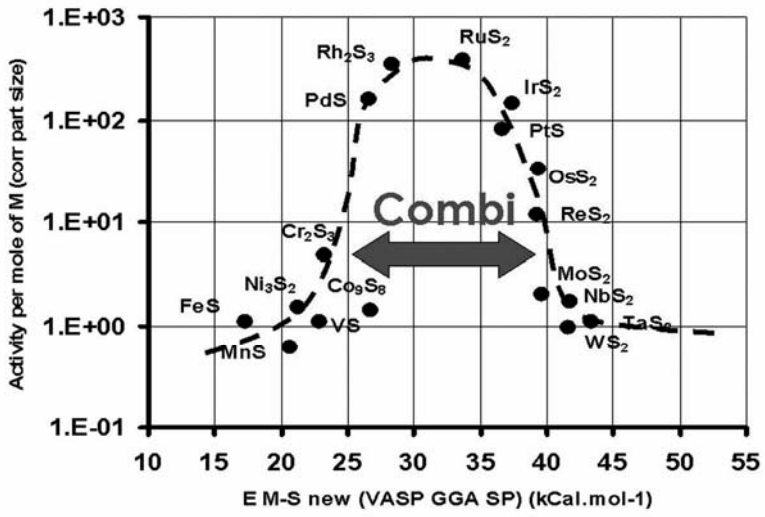

Fig. 12. Activity of metal sulfides in the catalytic hydrodesulfurization of dibenzothiophene vs. computed metal–sulfur bond strength. Experimental activity data are taken from Ref. 15

Researchers at the Institut Français du Pétrole (IFP) near Paris have developed a methodology, which tackles this challenge in an elegant and efficient way [16]. These researchers started with a concept initially proposed by Paul Sabatier at the beginning of the 20th century [17]. This principle states that a successful catalytic reaction of a molecule with a surface requires a binding between the molecule and the surface, which is neither too weak (the molecule would not stay on the surface long enough to react) nor too strong (the molecule would block the surface).

In the case of sulphur-containing molecules, it is plausible that the key interaction between the molecule and the surface is the metal–sulphur bonding. Now, if a molecule containing a sulphur atom binds to a metal atom at the surface of a sulphide, then the chemical environment of this metal atom resembles that of a bulk metal atom in that sulphide. This means that the bonding strength between a metal atom and sulphur of *bulk* sulphides contains information, which is pertinent to the catalytic activity.

To probe this idea, the researchers from the IFP under the leadership of H. Toulhoat formulated an approach to use electronic structure calculations to obtain bond strengths for systems such as transition metal sulphides. By taking experimental activity data as given in Table 3, for the bulk structures of the sulphides, they obtained a bond strength for each compound [16]. By plotting the catalytic activity as a function of this metal–sulphur bond strength, a remarkable correlation emerges in the form of a volcano curve (Fig. 12). Two classes of poorly performing catalysts emerge from this analysis. Some sulphides such as MnS bind too weakly and some compounds such as WS_2 too strongly.

Equipped with this understanding, the IFP researchers then proceeded to consider catalysts, which are combinations of sulphides from the left and the right of the peak

of the volcano. One such compound is MoS_2 combined with Co. In fact, Co-doped MoS_2 catalysts have been found earlier by empirical means and these catalysts are actually used in current processes. This validates the approach in a beautiful way. There is a large number of other possible combinations, which the current computational approach has identified, thus offering promising new candidates.

Table 3. Experimental activity data from Pecoraro and Chianelli [15] for the hydrodesulphurization of dibenzothiophene over transition metal sulphide catalysts

Metal sulphide	Activity	Metal sulphide	Activity
RuS_2	379.50	WS_2	3.20
OsS_2	216.30	NbS_2	1.70
IrS_2	171.80	Ni_3S_2	1.50
Rh_2S_3	106.10	Co_9S_8	1.40
ReS_2	39.40	VS	1.10
PtS_2	16.00	FeS	1.10
PdS	12.50	TaS_2	1.10
MoS_2	8.00	MnS	0.60
Cr_2S_3	4.80		

3. Perspectives

The current situation of computational materials science, which is illustrated by the examples discussed in this conference contribution, has opened the following exciting perspectives.

3.1. Computations have become a reliable source of materials property data

The accuracy of today's *ab initio* method has matured to a point, were properties including structural, mechanical and thermochemical properties can be calculated at a level of accuracy and reliability, which makes computations a viable source of primary materials property data. This capability is particularly valuable for systems such as point defects at low concentrations and interfaces, where experimental methods are difficult or impossible to perform. This use of computational materials science is likely to fill gaping holes in experimental data sets. For example, currently about 30,000 reliable crystal structures exist for known inorganic compounds. However, elastic constants for only several thousand are reported in literature. Computations can clearly help to fill this gap in a reliable, consistent, and cost-effective way.

3.2. Data and understanding derived from computations have the potential for breakthrough discoveries

As illustrated for the case of catalyst development, the combination of judiciously chosen physical and chemical concepts (e.g. Sabatier's principle), structural data-

bases, and *ab initio* total energy calculations on a series of compounds, new correlations and insight can be gained, which can guide the search for novel materials.

In the past, *ab initio* calculations have typically been performed for a single, or a few, systems at a time. This has provided detailed information of the electronic structure and energy potentials of these systems, thereby providing a deeper understanding of matter. With the current and future capabilities in terms of computational power, algorithmic efficiency, and automated computational software environments, large-scale investigations of hundreds or even thousands of compounds have become possible. This opens unprecedented and exciting perspectives. Systematic trends will emerge, which are not discernable from just a few systems. Possibly, systematic deviations between experimental data and computed values will reveal systematic shortcomings in the current level of theory, thereby helping to improve the accuracy of computational approaches. *Vice-versa,* erratic deviations between theory and experiment may also reveal problems in experimental data. A major benefit from such large-scale studies will be an increased confidence in the quality of computed and experimental data.

3.3. Connection of macroscopic continuum models with *ab initio* atomistic approaches

The traditional picture of connecting atomistic and macroscopic scales was a hierarchical approach. Quantum mechanical calculations feed into semi-empirical and force-field methods. These simplified computational approaches allow the simulation of larger systems over longer time scales, reaching mesoscopic eventually macroscopic dimensions. This type of "coarse-graining" is appealing and has worked to some extent in the simulation of biomolecular systems (proteins and DNA). However, attempts to use this approach in the field of inorganic materials has consistently run into the difficulties of generating transferable and reliable interatomic interaction parameters. It is possible, that in the field of inorganic materials such as metallic alloys, ceramics, and semiconductors, *ab initio* methods can be pushed far enough so that intermediate steps of simplified models can be skipped. In fact, this has been achieved in approaches such as the cluster variation methods. The calculations of elastic constants and thermochemical properties, as illustrated in the present paper, point in this direction. This direct link between *ab initio* and continuum models will be further facilitated by the growing interest in nanostructured materials. Current *ab initio* methods are operating on the nano-scale, at least as far as the length scale is concerned.

3.4. The industrial impact of computational materials science is growing

Given the current capabilities of computational methods, there is a worldwide growing interest by major industrial laboratories to employ computational materials

science as an integral part of their research and development efforts. This trend is very clear in Japan and in the U.S.A., whereas European companies tend to be more hesitant. Inevitably, this trend will increase the demand for carefully validated, highly robust, convenient, comprehensive, and well supported software systems. The trend will create new job opportunities for computational scientists, who are able to communicate effectively with materials engineers and who are able to formulate research strategies, which allow the efficient deployment of computational methods in solving industrial materials problems.

3.5. Computers are becoming a commodity

It is possible that the silicon industry will follow a similar trajectory in the 21st century as the steel industry did in the 20th century, namely transforming from a high-tech industry to a commodity business. As a consequence, the rate of computer hardware performance increase will start to taper off in the coming decades, but prices will continue to fall. This will unleash unprecedented computer power with thousands of processors and many terabytes of memory connected in single systems at affordable prices. Fault-tolerant software systems for large-scale computational jobs will be needed to harness this enormous computational power and therefore software will become the limiting factor in using this power. In order to anticipate this development, high-performance supercomputers are needed to enable the development and testing of algorithms and software systems, which in the future will run on low-cost computers.

The evolution of computational materials science depends on three factors, namely (i) fundamental theoretical concepts such as density functional theory and quantum Monte Carlo, (ii) computer programs which implement these concepts, and (iii) computer hardware, which allows the application of these programmes. These three factors evolve in very different time scales: fundamental concepts take of the order of 30-50 years to mature. Once introduced, they can change the field disruptively, as has been witnessed when DFT penetrated computational chemistry. Computer programs are developed and accepted by a larger community in the time frame of about 10 years. Computer hardware changes in 1–2 years.

There are significant consequences from these facts. It is very dangerous to develop software systems, which are dependent on a given generation of computer hardware. By the time the software is completed, the hardware will have changed. Fundamental changes based on the introduction of novel theoretical concepts take a long time, i.e. several decades.

4. Challenges for computational material science

A critical review of the current situation reveals the following key scientific challenges for computational materials science.

4.1. Accuracy of electronic energy

While computed structural properties are acceptable, there is an urgent need to improve the accuracy of electronic energies. This need becomes painfully obvious, if one tries to predict thermodynamic properties such as the melting point of a solid. The current level of standard *ab initio* calculations for solids, namely DFT-GGA, produces errors of the order of 100 K. This is very humbling. At the moment, it is not clear, which theoretical approach will improve this shortcoming. Will better functionals of DFT be sufficient, or will approaches such as quantum Monte Carlo be needed? Will they achieve the necessary accuracy or are entirely new approaches needed?

4.2. Better description of weak interactions

It is embarrassing that standard DFT-GGA methods are incapable of describing correctly the interplanar interactions in graphite or the interactions of two Mg atoms.

4.3. Unified computational approaches for multi-phase systems, e.g. solid–liquid

At present, solids, liquids, and molecules have their own optimal computational approach. Molecules are typically computed with Gaussian-type methods while solids are treated with plane wave approaches. Liquids such as water are described with force-fields. There is an urgent need for unified approaches, which will allow the description of systems such as solid/liquid interfaces, which play such an important role in areas such as corrosion and electrochemistry.

4.4. Novel approaches for reaction mechanisms

If one considers any industrially important chemical process, including combustion and corrosion, any attempt to use computational approaches face at least two major challenges, (i) these systems are ill defined and change with time and process conditions, (ii) there is an overwhelming multitude of possible chemical reactions that would need to be considered. At present, there are no generally practiced approaches that deal with these uncertainties and complexities. An attempt to use *ab initio* methods runs the risk of solving a highly idealized case, which may not even occur in a real system. Novel concepts are needed to deal with these complex systems.

4.5. Linking atomistic models with continuum models

There are many research opportunities to find better ways of linking atomistic approaches with continuum models. One of the challenges is simply communication between different scientific and engineering communities. To a large extent, scientists

and engineers working with finite element methods are not fully aware of the capabilities and approaches of computational materials science and vice versa. Interdisciplinary centres play a critical role in establishing communication channels between these communities, eventually leading to new and creative ways to combine these domains.

5. Conclusion

In conclusion, computational materials science is at an exciting stage of its development. Remarkable accomplishments have already been achieved, industry is starting to take notice, and powerful scientific and technological factors are fuelling the field. Thus, computational materials science is a vibrant and exciting field of growing importance.

Acknowledgments

It is my great pleasure to thank the many scientists and friends, who have directly or indirectly contributed to this paper. In particular, I want thank the scientists at industrial, governmental, and academic research laboratories, who are customers of Materials Design and whose commitment to the field remains a tremendous incentive. I also want to thank the scientific collaborators, especially Prof. Jürgen Hafner, Prof. Georg Kresse, Prof. Krzysztof Parlinski. My special thanks go to my colleagues at Materials Design, in particular Wolfgang Bergermayer (post-doc), Benoît Leblanc, Alexander Mavromaras, Paul Saxe, Hannes Schweiger (post-doc), Jürgen Sticht, and Walter Wolf. I also want to thank my long-term friend Prof. A. J. Freeman, who continues to have a passionate and inspiring commitment to the field of computational materials science.

References

[1] HOHENBERG P., KOHN W., Phys. Rev., 136 (1964), B864; KOHN W., SHAM L.J., Phys. Rev., 140 (1965), A1133.
[2] GUNNARSSON O., LUNDQVIST B.I., LUNDQVIST S., Solid State Commun.11 (1972), 149; VON BARTH J., HEDIN L., J. Phys., C 5 (1972), 1629.
[3] WANG Y., PERDEW J.P., Phys. Rev. B, 44 (1991), 13298; PERDEW J.P., WANG Y., Phys. Rev. B, 45 (1992), 13244.
[4] FOULKES W.M.C., MITAS L., NEEDS R.J., RAJAGOPAL J., Rev. Mod. Phys., 73 (2001), 33.
[5] WIMMER E., *Prediction of Materials Properties*, *Encyclopedia of Computational Chemistry*, P. von Ragué-Schleyer (Editor-in-Chief), Wiley, New York, 1998.
[6] BLÖCHL P.E., Phys. Rev. B, 50 (1994), 17953
[7] 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.
[8] LE PAGE Y.P., SAXE P., Phys. Rev. B, 65 (2002), 104104.
[9] MedeA 1.8, Materials Design, Inc., Taos, New Mexico, USA (2004) – www.materialsdesign.com
[10] YOUNG, G.A. JR., NAJAFABADI R., STROHMAYER W., BALDREY D.G., HAMM W.L., HARRIS J., STICHT J., WIMMER E., [in:] Proceedings of the 11th International Conference on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, Stevenson, WA (2003); see also www.osti.gov.
[11] WOLVERTON C., OZOLINS C., ASTA M., Phys. Rev. B, 69 (2004), 133109.

[12] PARLINSKI K., LI Z.Q., KAWAZOE Y., Phys. Rev. Lett., 78 (1997), 4063.
[13] BYLANDER B.M., KLEINMAN L., Phys. Rev. B, 41 (1990), 7868; SEIDL A., GÖRLING A., VOGL P., MAJEWSKI J.A., LEVY M., Phys. Rev. B, 53 (1996), 3764.
[14] GELLER C.B., WOLF W., PICOZZI S., CONTINENZA A., ASAHI R., MANNSTADT W., FREEMAN A.J., WIMMER E., Appl. Phys. Lett.,. 79 (2001), 368.
[15] PECORARO T.A., CHIANELLI R.R., J. Catalysis, 67 (1981), 430.
[16] TOULHOAT H., RAYBAUD P., J. Catalysis, 216 (2003), 63.
[17] SABATIER P., Beri. Deuts. Chem. Gesellschaft, 44 (1911), 1984.

Received 6 September 2004