relations between the spatial variations of the indium composition and those of the residual strain in InGaN films in InGaN/GaN multiple quantum wells (MQW) were simulated theoretically by this new method. The residual strains were found being able to be controlled significantly by selecting the pattern of composition fluctuation. The relation of the difference of the spatial pattern of the composition fluctuation to the dislocation density in InGaN/GaN MQW has been also discussed. In a typical case, $In_{0.5}Ga_{0.5}N$/GaN MQW structure with periodic composition fluctuation with period length less than 68 nm in InGaN layers seems to be able to be grown with no dislocation. In addition, the difference of the type of the short-range chemical ordering of the indium and gallium atoms, which must depend on the type of growth mode, was found to have a considerable influence on the stress distribution in InGaN films.

Keywords: *ab-initio* calculations, multilayer structures, residual stress strain

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Simulation of the para to ferroelectric phase transition in $BaTiO_3$: The role of domains

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$BaTiO_3$ - one of the most extensively technologically used ferroelectric material - undergoes successive phase transitions on lowering temperature, form cubic, to tetragonal, to orthorhombic, to rhombohedral. Different mechanistic models have been invoked over the years, among them the displacive model and the oder-disorder model, both suffering from some important disagreement with experiments [1]. To shed light on the microscopic mechanisms, we have performed molecular dynamics simulations on the para-to-ferroelectric phase transition in $BaTiO_3$ as well as subsequent transitions that involve polarization rotation. Therein, all degree of freedom are treated explicitly, including positions, cell geometry and temperature. For an unbiased mechanistic analysis, we employ the path sampling scheme, designed for activated processes and successfully applied in many previous works. Two main results are obtained: first, a detailed picture of microscopic displacements leading to domains, which do sum up to the correct macroscopic polarization and correspond very well with experiments. Second, the relevance and even the necessity of antiferroelectric arrangements [1], that naturally derive from nucleating the ferroelectric phase within the paraelectric phase and outlast in the orthorhombic one. Combination of ferro and antiferro regions results in far-from-obvious domain structures [2]. Simulation under the effect of an external field allow assessing the response of the material from multidomain to single domain, whereby antiferro arrangements play a key role. [1] Q. Zhang, T. Cagin, W. A. Goddard III, PNAS 103, 14695 (2006), [2] M. Pasciak, S. Leoni, Mater. Res. Soc. Symp. Proc. 1034E (2007), in press, [3] M. Pasciak, S. Leoni, in preparation.

Keywords: ferroelectric physics, ferroelectric phase transitions, molecular dynamics simulations

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Exploration of structures of phosphorus and calcium at high pressure using metadynamics simulation

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We predicted the structure of the phosphorus and calcium at high pressure which had been left unidentified after their powder X-ray diffraction patterns were reported. The X-ray experiment reported that the phosphorus has a new phase (P-IV) above the sc phase in the pressure region of 107GPa and 137GPa. After that some theoretical studies were made but they were not successful in predicting the structures of phosphorus which satisfactorily fit the X-ray pattern. We tried the first principles metadynamics simulation, which is a new theoretical method of finding the structures of local free energy minima. The structure of the P-IV we predicted was an incommensurately modulated structure[1] which was confirmed by an experimental group[2]. We then studied the calcium (Ca-IV and Ca-V) and found the structures of zigzag and helical modulations[3]. Both of the modulation periods were commensurate and the space groups of the structures are identified to be $P4_12_12$ and *Cmca*. These results will accelerate the study of the superconductivity of calcium in the phase V, of which the highest superconducting Tc in elements has been reported. We report the details of our studies of the exploration for those structures with some results of the studies for the origin of these modulated structures.

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Keywords: high pressure, simulation, metadynamics

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Cluster models for decagonal quasicrystals

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The model clusters specifying the sites for the constituent transition metals in the decagonal Al-Co-Ni and Al-Co-Cu quasicrystals have been proposed by comparing their electronic structures obtained by the x-ray emission and photoemission spectroscopic measurements [1] with those calculated by the discrete variational Xa potential (DV-Xa) method [2] on the basis of the reported electron microscopic data [3]. The experimentally observed electronic structures can be well explained by those of the model clusters. Their electronic structures show the pseudogap across the Fermi level in the Al partial density of states, which agrees well with a band structure calculation for the

approximant [4] and the Hume-Rothery mechanism for the formation of the quasicrystal [5]. For Al-Co-Ni, Ni and Co are located in the most inner and second inner parts, respectively, of the columnar model cluster, indicating the tendency of the close distribution of Ni atoms and the separated distribution of Co atoms. This is consistent with a recent study on the formation of the quasiperiodic Al-Co-Ni surfaces by the scanning tunneling microscopy [6]. The chemical bond and formation of the quasicrystals has been discussed in terms of local clusters around the transition metals.

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Keywords: decagonal quasicrystals, *ab-initio* cluster calculation, transition-metal clusters

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Ni(II) thiosemicarbazone complexes : Structural and theoretical investigation

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MM: Molecular Modelling DFT: Density Functional Theory Heterocyclic thiosemicarbazone and their metal complexes are among the most widely studied compounds for their potential antitumoral, antibacterial and antifungal activities (1). Some of these activities are closely related to the stability of molecular geometry (2) and especially when these activities are enhanced by the presence of some metallic ions (3). Therefore we were interested in single X-ray Crystallographic studies of some Ni(II) thiosemicarbazone complexes. These studies were supplemented by theoretical calculations (MM and DFT) in order to investigate more about the transmission of electronic effects between the redox unit and a metal center.

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Keywords: complexes, single-X ray diffraction, DFT

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Prediction and experimental determination of the crystal structure of $SiBr_4$

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The crystal structure of $SiBr_4$ is unknown hitherto, although the structures of all other EX_4 compounds (with E = C, Si, Ge, Sn, Pb and X = F, Cl, Br, I) are published. Possible crystal structures of $SiBr_4$ were predicted with force-field methods using the program CRYSCA[1]. Low-energy structures were post-optimised using the program package Cerius[2]. All calculations were performed with a Dreiding/X6 [2] force-field which was modified for Si-Br bond lengths. Calculations were performed in those space groups statistically most frequent for molecular compounds and for EX_4 compounds resp. $P1$ (Z = 1), $P\bar{1}$ (Z = 2), $P2_1$ (Z = 2), Cc (Z = 4), $P2_1/c$ (Z = 4), $P2_12_12_1$ (Z = 4), $Pna2_1$ (Z = 4), $Pca2_1$ (Z = 4) and $Pbca$ (Z = 8). In many cases higher symmetries (supergroups) were reached during the optimisation. Several possible polymorphs were found within an energy range of 5 kJ/mol above the global minimum. X-ray powder diagrams of $SiBr_4$ revealed the existence of two polymorphs; their structures were determined from X-ray powder data: the cubic high temperature phase crystallises in $Pa\bar{3}$ (Z = 8), the low temperature phase in $P2_1/c$ (Z = 4). Both phases had been predicted in the calculations.

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Keywords: lattice energy calculations, crystal structure prediction, crystal structure solution

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Computation of diffuse magnetic neutron diffraction single crystal patterns

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Magnetic diffuse scattering is observed in the paramagnetic state or in frustrated magnetic systems where long-range order is impeded by geometric constraints. This diffuse scattering can easily be probed using neutron diffraction and single crystal diffraction in particular allows to obtain very detailed maps in reciprocal space. The amount of information available from reciprocal space surveys of magnetic diffuse scattering can potentially give detailed insight into the interaction between the magnetic ions. Yet, very few such studies have been carried out likely due to the lack of software tools, methodology or computational resources. Here, we present Monte-Carlo simulations on model systems supported by experimental data. This allows phase diagrams to be explored and the effect of varying exchange constants to be simulated and compared to the data. Due to the finite size of the model crystal obtained, direct Fourier summation leads to noisy reciprocal space reconstructions. We have therefore extended the method of averaging over Fourier transforms of many small parts of the model crystal ('lots') to include magnetic diffuse scattering leading to high quality, smooth simulated patterns [1].

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