the US (LCLS), Europe (XFEL), Italy (FERMI), Japan (SCSS), Korea and China, as well as DUV-FELs in Germany (actually operational), France, UK, Italy and the US. She also gave details of the ARC-EN-CIEL project in France, which proposes an FEL down to around 1 nm. She summed up the deliberations of two meetings held in France focusing on the applications of such an FEL. These meetings have led to the development of a strong scientific case for a 4GLS in France, and some of the very impressive proposed applications were also discussed. R. V. Nandedkar gave an Indian perspective to fourth-generation sources, and pointed out that such a tool would revolutionize research in materials science, which has a very strong presence in India.

Towards the end of the workshop an evening session was organized on future FEL activities in India. Krishnagopal

briefed the participants that there was already interest in India in a fourth-generation light source. Some discussions have already taken place with scientists at IISc, TIFR, etc., in this regard, and a presentation was also given to SAC-PM in August 2005.

The view that emerged from the discussions was that a tunable, femtosecond, high-power laser in the X-ray regime would be a dream-machine that would open up revolutionary applications in science. A. Tadjeddine pointed out that even a short-wavelength FEL going down into the water-window region (4 nm) would engender tremendous applications in materials science, nanotechnology, chemistry, biology, medicine, condensed matter physics, plasma science, etc. S. K. Sarkar emphasized that the high-current, high-energy, electron beam needed to drive such an FEL would itself have many useful

applications in pulse radiolysis, neutron generation, plasma-based acceleration, etc., and would constitute a very important value-addition to any proposal.

The consensus was that a roadmap towards such an FEL, designed to deliver radiation in stages, should be developed immediately. At the same time, there needs to be wider deliberation within the user community on the advantages of a 4GLS to the Indian research community. The participants also cautioned that adequate attention needs to be paid to auxiliary facilities (conventional lasers, wet labs, diagnostic equipment, etc.) that will be needed by the users.

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RESEARCH NEWS

Crystal structure prediction – evolutionary or revolutionary crystallography?

S. L. Chaplot and K. R. Rao

It is a dream for material scientists to be able to predict the crystal structure of a material with given composition of elements under specific conditions of temperature and pressure. When this dream is realized it would be a boon in search for new materials of novel and exotic physical properties for a variety of applications. Recent work of Oganov and Glass[1] (Theoretical Mineral Physics Group of Eidgenössische Technische Hochschule [ETH] of Swiss Federal Institute of Technology, Zurich) seems to bring us close to achieving this dream. The group led by Oganov has been 'interested in the structure and properties of materials (mainly earth- and planet-forming materials) at high pressures and temperatures'. They perform theoretical studies using state-of-the-art *ab initio* simulation methods, 'ranging from atomistic to full quantum-mechanical, including such methods as *ab-initio* molecular dynamics and density-functional perturbation theory'

The ETH group has developed an evolutionary algorithm that enables random initial structures to evolve towards thermodynamically stable structures. They are able to reproduce known structures and predict new structures at high pressures in several elemental solids, for example, of oxygen, sulphur, carbon and nitrogen and of several molecular solids. The method requires calculation of free energy for any given structure. At present there are practical difficulties in calculating the free energy at high temperatures using *ab-initio* density-functional theory but this might be surmounted when more powerful computing resources become available. It is interesting to know how they carry out the evolutionary process. They start with a number (about 20 for a 10 atom unit cell) of randomly generated structures, given only the chemical composition of the material of interest, with no other experimental information; then they locally optimize and choose some of

those structures with low free energies to create the next generation of structures through ideas like heredity, lattice mutation and permutation of atoms. Heredity involves matching slices of parent structures. The next-generation structure is obtained by combining the fractional coordinates of selected atoms from two parent structures. In lattice mutation the unit cell is strained randomly. Certain hard constraints, such as ensuring reasonable bond lengths are used to guide the evolution process. So the evolution is based on evaluation of energetically favourable structures (the lower the total energy content of the crystal, the more favourably it is stable); the cycle is repeated with the favourably chosen structures till the most stable structure is arrived at. The fittest would survive.

Purely from considerations of geometry and packing, billions of different structures are possible even for a modest crystal with 10 atoms per unit cell. Evolutionary

algorithms along with hard constraints seem to be successful in leading to minimum energy structures. Oganov and Glass[1] claim that their method enables a global search for good structures, though it is not obvious as to how many generations the evolutionary process would require to reach the best structure with absolute minimum free energy. From test calculations, it is observed that for a, say, 20-atom system, one may need nearly 20 generations to arrive at the best possible structure with absolute minimum free energy. An example of evolution of a perovskite structure is given later. On the other hand, methods such as simulated annealing[2] and metadynamics[3] could be useful, although expensive, if one has a reasonable starting structure and one could explore neighbouring structures in the configuration space. Although success rates may be low, the simulated annealing method has been extensively used by others. Evolutionary methods could allow larger leaps in the configuration space. Evolutionary algorithms have been used before the recent work of Oganov and Glass but they were somewhat restrictive, for example, methods using a fixed unit cell[4] or applied to a single cluster[5] have been tried but these methods did not enable a broad enough search for crystal structures The new algorithm of Oganov and Glass enables a more efficient learning from previous generations.

Figure 1 provides an example from Oganov and Glass' work of how an optimum structure evolved in just 13 generations during evolution of a 20-atom unit cell of $MgSiO_3$ at a fixed pressure of 120 GPa and zero temperature. The resulting optimum structure, a post-perovskite phase, was previously simulated[6] and confirmed by experiments[6,7]. The post-perovskite phase is said to explain the anomalous properties of the D' region of the Earth. In fact, the perovskite structure obtained in the sixth generation was believed to be stable at high pressures in Earth's lower mantle. Oganov and Glass find the transition from perovskite to the post perovskite phase at 100 GPa that involves a change from corner sharing to edge sharing SiO_6 octahedral configuration. Secondly the ETH group has 'used *ab initio* metadynamics for the prediction of the plastic behaviour of $MgSiO_3$ perovskite and post-perovskite. This study has resulted in a new interpretation of seismic anisotropy of the Earth's D' layer'.

Temperature, besides pressure, has an important role in structure determination. The free energy $G(P, T)$ at a given pressure P and temperature T is given by the following expression in the quasi-harmonic approximation.

$$G(P, T) = E_{pot} + PV + E_{vib} - TS_{vib}, \quad (1)$$

where E_{pot}, E_{vib} and S_{vib} are the potential energy, vibrational energy (including the zero-point energy) and entropy respectively. The third and the fourth terms depend on temperature, and need calculation of the complete phonon spectrum. In terms of the phonon density of states $g(v)$, which itself would vary with pressure (P) and temperature (T) in the quasi-harmonic approximation, eq. (1) can be recast as

$$G(P, T) = E_{pot} + PV + \int dv\, g(v)\, [(hv/2) + kT \ln\{1 - \exp(-hv/(kT))\}], \quad (2)$$

where h and k are the Planck and Boltzmann constants respectively.

Oganov and Glass[1] have reported only zero temperature calculations, using the static enthalpy consisting of only the first and second terms in the above expression, since finite-temperature free energy calculations are expensive with the *ab-initio* methods they employed. Use of interatomic potentials is much less expensive[8,9] Free energies at moderate finite temperatures could be calculated in the quasiharmonic approximation. At very high temperatures, when anharmonicity is large, suitable thermodynamic methods are needed. But in this procedure, care is needed in selecting potentials that would be applicable over a wide range of pressures and temperature. We developed potentials for $MgSiO_3$ that reproduced the equation of state, thermal expansion, melting and phase transitions from low-pressure enstatite to high-pressure perovskite phases[10,11]. Since the post-perovskite phase has about 1% lower volume than the perovskite phase, the former may be expected to be more stable above a certain pressure.

The beauty of the evolutionary method is that such a post-perovskite phase did evolve while it was kinetically hindered in methods such as molecular dynamics simulation due to large energy barriers. The former method, however, does not provide information on mechanism of phase transitions that the latter method is capable of.

In addition to study of the perovskite $MgSiO_3$, Oganov et al.[12] have also studied the crystal structure of $CaCO_3$ under
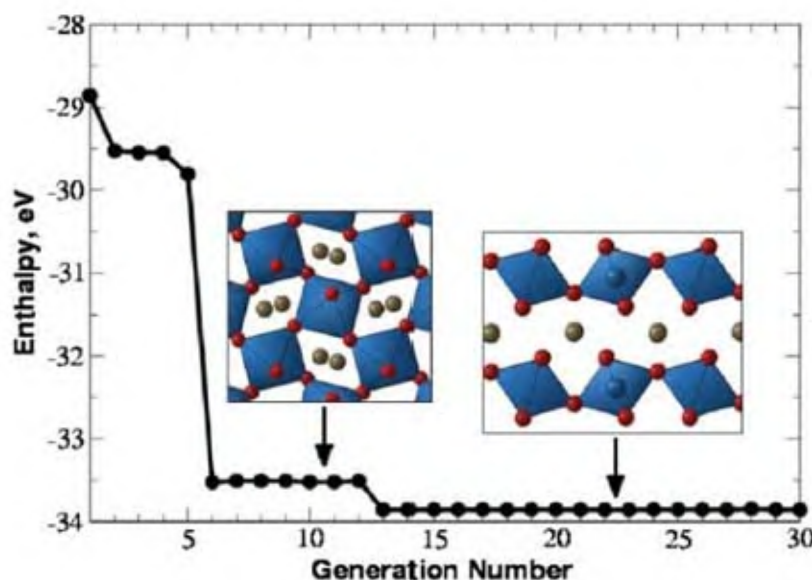

Figure 1. Prediction of the crystal structure of $MgSiO_3$ at 120 GPa with 20 atoms/cell. Enthalpy per 20 atoms of the best structure as a function of generation. Insets show the perovskite and post-perovskite structures (blue polyhedra – SiO_6 octahedra; gray spheres – Mg atoms). Between 6th and 12th generations the best structure is perovskite, but at the 13th generation the post-perovskite structure is found. [Reprinted with permission from Oganov, A. R. and Glass, C. W., *J. Chem. Phys.*, 2006, **124,** 244704. Copyright 2006, American Institute of Physics.]

conditions corresponding to the pressure of Earth's mantle. The aragonite structure formed at high pressure undergoes a crystallographic structure transformation to a post-aragonite structure beyond 40 GPa as per theoretical predictions. This has been borne out by 'the experimental powder diffraction pattern above 42 GPa' (Figure 2). They predict, further, a new structure beyond 137 GPa.

Another series of structures examined by ETH group relates to (Mg, Fe) SiO_3. Based on this work, 'they have predicted a new family of mantle minerals. These discoveries shed new light on the plastic flow of mantle rocks inside our planet – the process that controls plate tectonics and the associated earthquakes, volcanism, and continental drift'[14]. Further, as already stated, Oganov and Glass have been able to predict many interesting new high-pressure phases in a number of elemental systems (of C, N, O and S) and a few more complex solids. These include a post-diamond structure of carbon above 1000 GPa. A red-oxygen phase was found experimentally[15,16] earlier but its structure was uncertain. Oganov and Glass conclude that the red-oxygen phase contains O_4 units in agreement with ref. 17, but seems to be metastable. They predict
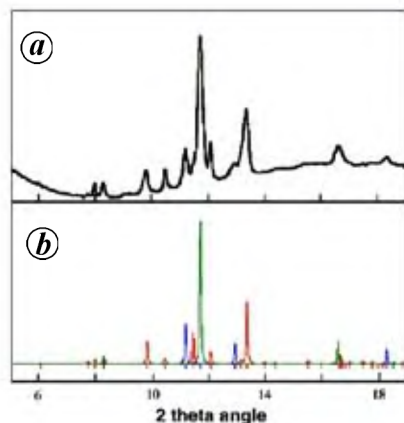
the stable structure consisting of O_2 molecular chains (Figure 3). Both the oxygen structures are not found for any other element so far. However it seems that, when pushed to the extreme, the *ab-initio* density functional theory with today's approximations, may have its limitations (Oganov, A. R., Private communication).

Oganov and Glass also find many metastable structures that provide an understanding of chemical bonding most likely to occur at a given pressure. The various examples they reported indeed provide a testimony to the huge capability of their evolutionary algorithm in crystal structure prediction.

The ETH group is involved in improving upon their software USPEX (Universal structure predictor: Evolutionary Crystallography) that may be able to predict 'structures containing hundreds or perhaps even thousands of atoms per unit cell'. However it may not be soon that
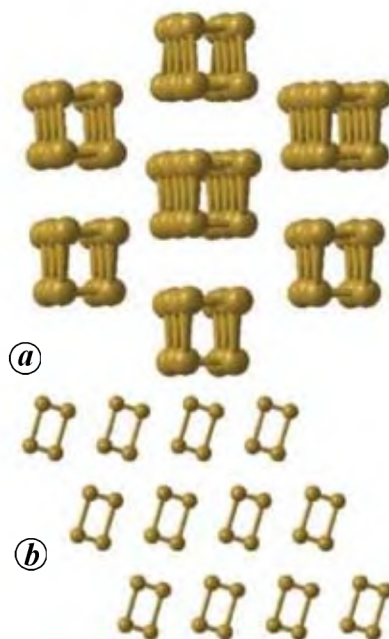
'the crystallographers (would become) redundant', with these revolutionary aspects of predicting crystal structures through an evolutionary path.

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Figure 2. Comparison of (*a*) observed[13] and (*b*) calculated X-ray diffraction patterns of the post-aragonite phase of $CaCO_3$ for samples quenched to 36 GPa (red peaks – post-aragonite; green–NaCl; and blue–Pt). Reprinted with permission from Oganov, A. R., Glass, C. W. and Ono, S., *Earth Planet. Sci. Lett.*, 2006, **241**, 95–103.

Figure 3. Structures of oxygen identified by USPEX at 25 GPa: (*a*) stable O_2 chain structure and (*b*) metastable structure with O_4 groups consisting of pairs of O_2 molecules (higher in enthalpy by 7 meV/at.). Reprinted with permission from Oganov, A. R. and Glass, C. W., *J. Chem. Phys.*, 2006, **124**, 244704. Copyright 2006, American Institute of Physics.