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An X-ray constrained wavefunction (XCW) is a wavefunction constrained to reproduce the structure factors from X-ray charge density experiment [1]. XCW's have primarily been used to obtain accurate images of the electron density in molecular crystals [1]. In this talk the XCW method is extended to the calculation of linear and non-linear optical response properties for several molecular crystals [2]. The theory used for the calculation of bulk (crystalline) susceptibilities and refractive indices from molecular polarisabilities will be reviewed. Results for several systems will be presented and discussed. I will also outline a method for improved structure determination based on using aspherical atomic densities obtained from quantum mechanical calculations. The new method allows the determination of ADP's for hydrogen atoms from the X-ray data alone [3]. The possibility of using such aspherical densities in everyday structure refinement will be discussed.

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MS.37.3

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Characterization of weak chemical bonds in highly strained and hypervalent compounds

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To characterize chemical bonds in highly strained and hypervalent compounds have been attractive target of theoretical study. However, it is not rare that some researcher derive different result from other researchers, who study the same compound, especially for such weak chemical bonds. While, if such compounds are synthesized and crystallized, we can perform charge density analysis using accurate X-ray diffraction data, which shows electron density distribution as it is. We report here bonding characters of strained cyclopentyne and 5- and 6-coordinate carbon compounds. Small cyclic alkynes are, in general, unstable because of ring strain. Recently, 1-zirconacyclopent-3-yne complexes, viz 5-membered cyclic alkynes, were synthesized and crystallized.[1] The experimental electron density analysis clarifies that both of the eta2-pi,pi and eta4-pi,pi structures contribute to the bonding not only the former structure.[2] In the case of the 5- and 6-coordinate carbon compounds, we showed dative character of the hypervalent bonds.[3, 4]

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How and why elemental boron undergoes self charge transfer between 19 and 89 GPa

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Boron has nearly 20 polymorphs with non-trivial chemical bonding, complex structures and similar energies. It is the only light element for which the ground state is not experimentally established at ambient conditions. Using high-pressure experiments and an *ab-initio evolutionary methodology*, the structural stability of boron under pressure was explored.¹ At low pressures (<19 GPa) boron adopts covalent structures based on icosahedral B₁₂ clusters, and at high pressures (>89 GPa) it forms a superconducting α -Ga-type phase. At intermediate pressures a *new insulating phase*, γ -B, has been found to be stable.¹ Its structure consists of distorted B₁₂ clusters and B₂ pairs: (B₂)^{Δ+}(B₁₂)^{Δ-}, with a significant charge transfer (CT), substantiated by several theoretical measures and physical properties. Using Bader's theory, δ amounts to ≈ 0.34 - 0.48 , based on either PAW or DFT-LCAO densities. Electron charge flows from B₂ to B₁₂ units for their corresponding frozen 3D sublattices act as *n*-doped and *p*-doped semiconductors, respectively. The CT occurring in this unique phase affects its physical properties (electronic band gap, infrared absorption, dielectric properties, etc.) and results from the Lewis acid-base interaction of the B₁₂ and B₂ groups. It is the ability of boron to form clusters with very different electronic properties and the very low packing efficiency of icosahedral structures (34% for α -B₁₂) which leads to γ -B, the *first experimentally established autoionized form of an element*. An analysis of bonding within and between the B₂ and B₁₂ subunits and its relationship with the observed CT in γ -B is also outlined.

¹A.R. Oganov, J. Chen, C. Gatti, Y.-Z Ma, *et al.*, Nature submitted

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Advances in quantum *ab initio* calculations with the CRYSTAL code

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The electronic structure and properties of crystals can be calculated *ab initio* with CRYSTAL at different levels of approximation ranging from Hartree-Fock (HF) to Kohn-Sham (KS) Density Functional Theory and including use of hybrid functionals. Expressing the crystalline wavefunction in terms of linear combinations of atomic orbitals (LCAO) allows easy interpretation of the electronic structure and direct comparison with molecular fragments. The release of the code presently distributed, CRYSTAL06 (<http://www.crystal.unito.it>), enables fully automated and efficient search for minimum energy structures and the computation of a variety of properties including structural, elastic, piezoelectric, dielectric, magnetic and electronic properties, and the simulation of vibrational spectra. Extensive use of symmetry, in both the real and reciprocal space, and low computational requirements make the program efficient and suitable for the study of complex structures with ordinary computer facilities. Recent achievements in the parallelization of the code and use of parallel linear algebra libraries now permit large-scale calculations for systems containing thousands of atoms in the unit cell with good scalability over thousands of processors on High Performance Computers. New developments also involve an efficient implementation of the Coupled-Perturbed (CP) HF/KS equations for the calculation of linear and nonlinear optical properties of insulators and semiconductors (electron polarization, dielectric and hyperpolarizability tensors). Application of the CPHF/CPKS method to the analytical calculation of various properties such as the piezoelectric tensor, infrared and Raman intensities is under development. The new features will be illustrated through examples of application.

Keywords: *ab-initio* periodical and cluster calculations, crystal structure and properties, DFT

MS.38.1

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Phase field modeling of self-organized polycrystalline structures: Denrites, spherulites, eutectics

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Recent advances we made recently in phase field modeling of polycrystalline self-organized structures will be reviewed. Self-organized crystalline patterns are present in a variety of systems including metals, polymers, minerals, and biological systems. The fact that similar polycrystalline patterns are seen in systems of very different molecular structure suggests that a minimal model based on coarse-grained fields, which neglects details of the molecular interactions, might be feasible. Along these lines, we have developed a phase field models of polycrystalline solidification that rely one or more orientation fields in representing crystallographic orientation. Our models have been applied for describing various self-organized structures including dendritic morphologies, disordered dendrites, spherulites, and eutectic structures in 2D and 3D. Our models consist of several mechanisms for nucleating new grains at the perimeter of the crystallites, including homogeneous and heterogeneous processes. It will be shown that a wide range of observed polycrystalline morphologies can be reproduced by varying only a few model parameters. Preliminary results for modeling dendritic and eutectic self-organization in an atomistic phase field theory (the phase field crystal model) will also be presented.

Keywords: self-organization, phase field theory, polycrystals

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High temperature characteristics of unidirectionally solidified ceramic eutectics

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We have recently developed ceramic eutectics, which are named Melt Growth Composites (MGCs). The binary MGCs (Al_2O_3 /YAG and Al_2O_3 /GAP binary systems) have a novel microstructure, in which continuous networks of single-crystal Al_2O_3 phases and single-crystal oxide compounds (YAG or GAP) interpenetrate without grain boundaries. To characterize the entangled structure of the typical MGCs, the X-ray computerized tomography (micro X-ray CT) was performed at a synchrotron radiation facility Spring8. The micro X-ray CT showed that the Al_2O_3 and the YAG are entangled with each other. Therefore, the MGCs have excellent high-temperature strength characteristics, creep resistance, superior oxidation resistance and thermal stability in the air atmosphere at very high temperatures. In the paper, high temperature characteristics of MGCs such as high temperature strength (Fig. 1), creep resistance, oxidation resistance and thermal stability of microstructure, and structural characteristics of the typical MGCs will be briefly introduced.

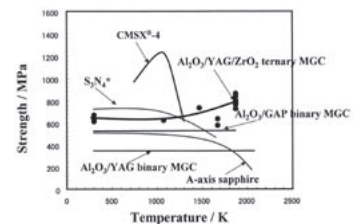


Fig. 1 Temperature dependence of strength of Al_2O_3 /YAG, Al_2O_3 /GAP binary and Al_2O_3 /YAG/ ZrO_2 ternary MGCs.

Keywords: high-temperature ceramics, single crystal, mechanical properties

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Nanoparticle halo formation around colloids in binary solutions

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Colloidal suspensions are widely used in applications such as photonic crystals and coatings, where nanoparticle engineering is a new model whereby interactions may be regulated to provide control over suspension stability. One such stabilizing mechanisms is nanoparticle “haloing.” This colloidal stabilization mechanism has been predicted theoretically and inferred experimentally in microsphere-nanoparticle mixtures that possess high charge and size asymmetry. The term “halo” implies the existence of a non-zero separation between the highly charged nanoparticles and the negligibly charged microspheres that they surround. For the first time, we were able to quantify this nanoparticle-microsphere particle

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