SYMPOSIUM B

Computational Approaches to Predicting the Optical Properties of Materials

November 30 – December 2, 1999

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*Invited paper
SESSION B1:  
Chair: Steven G. Louie  
Tuesday Morning, January 30, 1990  
Room 209 (H)  

8:30 AM  #B1.1  
Photoluminescence upconversion spectroscopy: A new technique to study type II band-offsets at semiconductor heterojunctions.  
P. Y. Yu, Department of Physics, University of California, Berkeley, and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA; G. Martinez, J. Zeman, Grenoble High Magnetic Field Laboratory, MPRK/UCNRS, Grenoble, FRANCE; and K. Uchida, Department of Communications and Systems, The University of Electro-Communications, Tokyo, JAPAN.  

Photoluminescence upconversion is the phenomenon in which a single exciton emits photons with energy higher than that of the excitation photon. This effect has been observed in many materials including rare earth ions doped in insulating hosts and semiconductor heterostructures using high-power lasers as the excitation source. Recently this effect has been observed also in partially CdGeCdP-ordered GaInP epilayers grown on GaAs substrates. Using the fact that the pressure coefficient of electrons in GaAs is higher than those in GaInP we have been able to “manipulate” the band-offset at the GaInP/GaAs interface. By converting the band-offset from Type I to Type II we were able to demonstrated that the efficiency of the upconversion process is greatly enhanced by a Type I band-offset. Furthermore, by using the magnetic field of the electrons as a “yardstick” within this resolution we have been able to determine the size of Type II domains in GaInP near the interface. By combining high pressure and high magnetic field measurements we were able to show how the Type II domains increase in size under high pressure. Acknowledged support at Berkeley was supported by the DOE through contract DE-AC03-76SF00098. The Grenoble High Magnetic Field Laboratory is “Laboratoire conventionné au LUF” et INPG de Grenoble”, J. Uchida was supported by a grant ERRCHEGC 92/035 from the European Commission, Grant 202/96/0021 from the Grant Agency of the Czech Republic and Grant A10118/09 of the Academy of Sciences of the Czech Republic. We also like to acknowledge collaborations with Z.P. Su, K.L. Teo, and S. Julian.  

9:00 AM  #B1.2  
Comparison between theoretically and experimentally determined optical spectra of tetrahedral semiconductors.  
Maurer Cardona, Max-Planck-Institut für Festkörperforschung, Stuttgart, GERMANY.  

The state of the art of ab initio optical constants calculations, as discussed in this symposium, has reached a high degree of sophistication in the past few years. Nevertheless, exact calculations apply only to electronic effects for a rigid lattice, disregarding electron-phonon interaction effects which are present even at T = 0. To minimize such problems, calculations should, at least, be compared with measurements at T = 0. Recent measurements with different isotopic masses have led to an in-depth confrontation of the model states making possible, in principle, the elimination of phonon self-energies from the optical spectra measured at room temperature. Comparison of theoretical with experimental spectra leads to discrepancies that must be attributed to inadequacies in the computational codes. Such state-of-the-art codes are rather cumbersome and have been only applied to simple crystals (mostly tetrahedral semiconductors). They have not yet been used for the calculation of spectra related to higher-order phenomena, such as nonlinear susceptibilities, piezooptic functions, and Raman tensors. In these cases, semiempirical calculations of various degrees of sophistication, including sometimes analytical expressions, can be used to interpret experimental data. Semiempirical methods can also be used to calculate the effect of electron-phonon interaction on the optical spectra (as observed through the dependence of optical spectra on temperature and isotopic masses). Examples of calculations of the spectral dependence of piezooptic functions and Raman tensors will be presented.  

9:30 AM  #B1.3  
Correlated magnetoelectrons in semiconductor quantum dots at finite temperature.  
D.J. Dean, M.R. Strayer, Physics Division, Oak Ridge National Laboratory, Oak Ridge, TN; J.C. Wells, Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN.  

We describe computational methods for the theoretical study of explicit correlations beyond the mean-field in excitons confined in semiconductor quantum dots in terms of the Auxiliary-Field Monte Carlo (AFMC) method [1]. Using AFMC, the many-body problem is formulated as a Feynman path-integral at finite temperatures and evaluated to numerical precision. This approach is ideally suited for implementation on high-performance parallel computers. Our strategy is to generate a set of mean-field states via the Hartree-Fock method for use as a basis for the AFMC calculations. Response functions are calculated at finite temperature to study the effects of exciton-carrier and exciton-exciton correlation. As an application, we compute the exciton spectrum, specific heat, and the critical temperature for the symmetry-breaking phase transition in two-dimensional quantum dots. [1] S.E. Koonin, D.J. Dean, and K. Langwies, Phys. Rev. B33, 1 (1992).  

9:45 AM  #B1.4  
Density functional study of ZnGeP2 and CdGeAs2: electronic structure under hydrostatic pressure.  
Peter Zagal, Materials Science and Chemistry Division, Argonne National Laboratory, Argonne, IL.  

The ternary semiconductor compounds ZnGeP2 and CdGeAs2 are non-linear optical materials which are particularly promising for future laser applications. CdGeAs2 has a direct bandgap of 1.8 eV while the pseudodirect nature of the band gap in ZnGeP2 remains an open question. It has long been known that the pressure coefficients of forbidden energy gaps in chalcopyrites are dependent on the nature of the band gap. Crystals with pseudodirect gaps have a small positively or negatively sloped absorption edge while direct gap chalcopyrites such as CdGeAs2 have a large positive slope. We performed density functional calculations using Gaussian orbital basis sets for CdGeAs2 and ZnGeP2 crystals. Structural parameters were optimized for several different unit cell volume values. Total energy vs volume dependencies were used to obtain equations of state. Energies of the top states in the valence band and the bottom states in the conduction band of T, P, and N points were calculated to be linear functions of volume. Pressure coefficients of forbidden gaps were derived from these results and compared to experimental data.  

10:00 AM  #B1.5  
Pseudopotentials and optical properties.  
Marvin L. Cohen, University of California at Berkeley, Dept of Physics, and Lawrence Berkeley National Laboratory, Materials Sciences Division, Berkeley, CA.  

In the 1960's and 1970's the basic problem of explaining the optical properties of semiconductors in the visible and UV was essentially solved using semi-empirical pseudopotentials. A worldwide theoretical-experimental collaboration focused on interpreting optical structure in terms of interband transitions. The electronic band structures and response functions for reflectivity, absorption, photoemission, and modulated reflectivity experiments were determined using the EPM (empirical pseudopotential method). The results for dozens of semiconductors illustrated not only the power of the method, but also supplied useful data and yielded general interpretations of electronic properties. The semiempirical approach gave reliable electronic density maps and slowly evolved into a first-principles method. This evolution and the origins and applications of the methods will be described.  

11:00 AM  #B1.6  
Application of the time-dependent local density approximation to the optical properties of atoms and clusters.  
Igor Vasiliev, Sandor Ought, and James R. Chelikowsky, Department of Chemical Engineering and Materials Science, University of Minnesota and Minnesota Supercomputing Institute, Minneapolis, MN.  

Ab initio excitation energies and photoabsorption spectra of atoms, metallic and semiconductor clusters are computed within the time-dependent local density approximation (TDLDA). The TDLLDA formalism is implemented entirely in real space. Our calculations demonstrate that TDLLDA technique is accurate and, when applied to clusters, is more efficient than alternative methods. In all cases explored, we find the calculated excitation and absorption gaps to be in good agreement with available experimental data. For gullium arsenide clusters our calculations predict clearly distinguishable spectra for clusters with different structures, which may help to identify isomers. The calculated spectra for clusters exhibit long absorption tails extending deep into the region of the lower transition energies. Such behavior can be attributed to the existence of free surfaces in clusters.  

11:15 AM  #B1.7  
Response of semiconductors and fullerenes to ultrashort and ultra-intense laser pulses.  
Traun Dumitricu, Ben Tornabene and E. Allen. Texas A&M University, Dept. of Physics, College Station, TX.  

The interaction of matter with fast intense laser pulses is a current frontier science. This talk will emphasize semiconductors and fullerenes, with some discussion of other molecules. We have
performed simulations which show in detail how both electrons and
atoms respond to fast intense laser pulses (with durations of order
100 fs and intensities of order 10^12 W/cm^2, or about one trillion
centimeter). Above a threshold intensity, which results in promotion
of about 10% of the electrons to the conduction band for GaAs, and
15% for Si, the semiconductor lattice is destroyed and the band gap
collapses to zero. The threshold is approximately the same for GaAs
and Si at a photon energy of 2 eV, because Si has a stronger bond
but a higher population of excited electrons. We have also performed
simulations of the response of C60 and other fullerenes. We observe
a symmetric excitation of electrons which reflects the intramolecular
bonding. As a result, there is a vibrational excitation which is almost
purely in the breathing mode at low temperature. At the highest
fluence for which the molecular remains intact, the vibrational
amplitude is very large, with the molecule oscillating between about
7.2 and 8.8 Ångstroms. Still higher fluences produce photodissociation,
with the evolution of carbon dimers.

The technique employed in the simulations is a tight-binding-electron
 dynamics. Using a time-dependent Poisson substitution, one can treat
the coupling of electrons to an arbitrarily strong radiation field
without the need for any additional parameters. The atomic dynamics
is solved with the velocity Verlet algorithm, and the electronic
 dynamics with a Car-Parrinello algorithm. Both the time-dependent dielectric function ε(ω) and the time-dependent second-order susceptibility
χ(2)(ω) are monitored during a simulation for the semiconductors,
and the results are in good agreement with the experimental
observations of these quantities.

1:30 PM *B1.8
CRITICAL MICROSCOPIC PROCESSES IN SEMICONDUCTOR LASERS.
M. S. Hybertsen, M. A. Alam, G. A. Baraff and R. K. Smith,
Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Operation of semiconductor laser diodes with multiple quantum wells
in the active region is dependent on several microscopic processes.
These include capture of carriers into the quantum wells, cooling of
the injected carriers, non-radiative recombination of carriers in the
quantum well, and the optical gain in the quantum wells which leads
to stimulated emission. Each of these processes presents a
fundamental challenge for theoretical analysis. Furthermore,
experiments probe a non-trivial combination of these processes. An
integrated laser simulator has been developed which includes carrier
transport, quantum-mechanical treatment of the quantum wells, and
the optical field in a self-consistent analysis of the laser diode.
The simulator allows direct comparison to experimental data and analysis
of the impact of the various microscopic processes on the operation of
the device. For example, an accurate model for the optical gain,
including a proper treatment of the broadening, must be combined
with the details of the transport of carriers through the multiple
quantum well region to understand the measured optical spectra.

SESSION B2
Chair: Eric L. Shirley
Tuesday, November 30, 1999
Room 209 (H)

1:30 PM *B2.1
OPTICAL SPECTRA OF SURFACES AND POLYMERS FROM
FIRST PRINCIPLES. Michael Rohlfing, Universität Münster, Institut
für Theoretische Physik II, Münster, GERMANY.

We present a novel approach of calculating the optical excitations
of semiconducting systems from first principles [1]. To this end, we first
solve Dyson’s equation for the one-particle Green’s function, yielding
the quasiparticle excitations of the system. The electronic self-energy
operator is calculated within the GW approximation. Thereafter, we
solve the Bethe-Salpeter equation for the two-particle Green’s
function of coupled electron-hole pairs, fully including the
electron-hole interaction. This allows us to investigate both bound
excitons and resonant electron-hole excitons and to evaluate the
entire optical spectrum. We employ this technique to investigate the
optical spectra of low-dimensional systems [2]. In the case of
conducting polymers, we show that the electron-hole interaction
dramatically alters the absorption spectrum which is dominated by
exciton states at energies below the fundamental band gap. The
analysis of the corresponding-electron-hole-pair excitations yields
detailed insight into the spatial correlation between the electron and
the hole. In case of the two-dimensional electron- and hole-gases, the
differential reflectivity spectrum is dominated by a surface exciton formed
from the p-bonded surface states. The excitonic binding energy is more
than one order of magnitude larger than in bulk Si. [1] M. Rohlfing

2:00 PM *B2.2
AB INITIO CALCULATIONS OF RESPONSE PROPERTIES
INCLUDING THE ELECTRON-HOLE INTERACTION.
Lucin Reining, Venerio Olevano, Stefan Albrecht, Madeleine Meyer,
Laboratoire des Solides Irradiés, Ecole Polytechnique, Palaiseau,
FRANCE; Rodolfo Del Sole, Giovanni Onida, INFN, Dip. di Fisica
dell’Università Tor Vergata, Roma, ITALY.

We discuss the current status of a computational approach which
allows to evaluate the dielectric matrix, and hence electronic
excitations like optical properties, including excitonic effects.
We present recent numerical developments and discuss the points
which might be critical in practical applications. We will present recent
applications of the method, focussing our interest on several oxides.
These are materials where the experimental data yield the
electron bandstructure in a more direct way, like photosensitisation.
However, the results are less compared to available absorption spectra. It is
therefore crucial to go towards a quantitative description of these
properties. We will show how this can be achieved, and how the ab initio
calculations can yield additional information, like e.g. the localization
of the electron-hole pair.

1 G. Onida et al, Phys. Rev. Lett. 75, 818 (1995); S. Albrecht et al,
2 Other approaches are also used in L.X. Benedict et al, Phys. Rev.
B 57, R5385 (1998); Phys. Rev. Lett. 80, 4514 (1998); and M.

2:30 PM *B2.3
PHOTODISSOCIATION OF OXYGEN DEFICIENT DEPOSITS IN
SILICATE AND GERMANOSILICATE GLASSES.
Krishnan Raghunathan, Bell Laboratories, Lucent Technologies,
Murray Hill, NJ.

We have investigated the structural and electronic properties of
oxygen deficient deposits in silicate and germanosilicate glasses by ab
initio quantum chemical studies using a cluster approach. In
particular, the photodissociation and photoluminescence properties of
several competing defect models have been evaluated using accurate
cluster calculations. The performance of methods such as gradient-corrected density functional theory for the accurate
evaluation of electronic excited states is assessed. The influence of the
basis set and cluster size on the calculated electronic properties is
explored. The effect of Ge on the relative thermodynamic stabilities of
the defects is examined. Careful comparisons are performed with the
known experimental information on the photodissociation and
subsequent photoluminescence in silicate and germanosilicate glasses.

2:45 PM *B2.4
QUASIPARTICLE EXCITATIONS, EXCITONS, AND OPTICAL
ABSORPTION IN ALPHA QUARTZ. Eric Chang, Michael Rohlfing,
and Steven G. Louie, Univ of California at Berkeley, Berkeley, CA.

We have investigated the optical absorption spectrum of SiO2 using a
first-principles approach, including quasiparticle self energy and
electron-hole interaction effects. The quasiparticle band structure of
crystalline SiO2 in the alpha quartz phase is calculated within the
GW approximation, and the optical properties are obtained by solving
the Bethe-Salpeter equation for the excitonic spectrum and
wavefunctions. We discover features qualitatively different from those
of Effective Mass Model in these optical excitations, which reveal
a rich structure in the spatial and resonance character of the excitonic
states. The optical absorption spectrum in an energy range of 0-25 eV
is calculated, and very good agreement with experiment is obtained.
We compare the 2p-electron results computed using wavefunctions
and spectrum obtained from the Bethe-Salpeter equation to the
one-particle interband transition results computed ignoring
electron-hole interaction, and identify which peaks in the absorption
are attributable to excitons and which to interband transitions.

3:30 PM *B2.5
THE ELECTRON-HOLE INTERACTION AND LINEAR OPTICAL
CONSTANTS. Lorin X. Benedict, LLNL, Livermore, CA.

The intrinsic electron-hole interaction has an important effect on the
linear optical constants of most materials. I will highlight its
importance by discussing three topics in the theory of optical
properties: 1) a time-dependent picture of optical absorption which
helps to explain the relative strength of excitons and interband
effects in different systems; 2) the polarization dependence of the optical constants of
wurtzite GaN and AlN; and 3) ongoing work to extend present
computation techniques to highly excited electronic systems, in an
effort to understand the results of short-pulse pump-probe laser
experiments.

4:00 PM B2.6
COMPUTATIONAL ALLOY APPROACH TO ALLOY
THEORETICAL APPROACHES TO SURFACE SECOND HARMONIC GENERATION. J. Mejia, Fernando Mendez, Centro de Investigaciones en Optica, León, México, M. Palumbo and R. Del Sole, Rome University II, Leon GTO, MEXICO.

We apply ab-initio methods and the semiempirical tight binding approach, to calculate the second harmonic generation at various surfaces of organosymmetric semiconductors. We show that both methods give similar results. We compare our calculations with the available experimental results investigated so far, and show an excellent agreement.

SESSION B3
Chair: James R. Chelikowsky
Wednesday, Morning, December 1, 1999
Room 309 (H)

8:30 AM *B3.1
OPTICAL PROPERTIES OF SILICON QUANTUM DOT S: SURFACE AND BULK ELECTRONIC STATES.
Philippe M. Fauchet, University of Rochester, Dept. of Electrical and Computer Engineering, Rochester, NY.

The optical properties of direct-gap semiconductor quantum dot states have been fully characterized and can be explained satisfactorily by theory. In contrast, the optical properties of silicon quantum dot states have not been investigated. In this presentation, we report experiments that establish how the photoluminescence of these objects is affected by the quantum dot size and the choice of the surface bonds. These results are compared to theoretical calculations that provide a microscopic understanding of the electronic states that exist in and on these dots.

9:00 AM *B3.2
OPTICAL PROPERTIES OF SILICON NANOCRYS TALS: A FIRST PRINCIPLES STUDY.
Serdie Ogut, Department of Chemical Engineering and Materials Science, Minnesota Supercomputing Institute, University of Minnesota, Minneapolis, MN.

Ab initio quasiparticle gaps, self-energy corrections, exciton Coulomb energies, and optical gaps of Si nanocrystals are calculated using the high-order finite difference pseudopotential method. The calculations are performed in real space on hydrogen-passivated Si clusters with diameters up to Å (100 atoms). Different computational techniques, such as total energy differences from density functional theory within the local density approximation (LDA) and optical spectra using time-dependent LDA are utilized to make systematic comparisons with experimental data. We show that the size-dependent self-energy correction is enhanced substantially compared to bulk, and quantum confinement and reduced electronic screening result in appreciable excitonic Coulomb energies. Calculated optical gaps are in very good agreement with experimental absorption data from Si nanocrystals.


9:30 AM B3.3
TIME-DEPENDENT EXCITON CORRELATIONS IN NANOSCALE QUANTUM DOT S.
Lars Jonson, Ohio State Univ, Dept Physics, Columbus, OH.

In nanoscale quantum dots, subpicosecond laser pulses can induce and probe strong time-dependent Coulomb correlations between confined electrons and holes. Correlation dynamics for one or two electron-hole pairs driven by both interband and intraband lasers can be simulated by numerical solution of the time-dependent Schrodinger equation within a configuration-interaction description. For example, Coulomb correlations of two electrons and two light holes in a 5x5x2.5 nm3 GaAs quantum dot yield strong oscillations in the luminescence. Pure correlation effects are revealed by a carefully chosen sequence of three circularly polarized pulses. For these calculations, Coulomb and electron-laser matrix elements were calculated within the effective-mass approximation with infinite potential walls. For a quantum dot with an internal dielectric barrier that splits the energy level on the 10 ns scale, correlation effects couple the interband and intraband optical response. Work in progress aims at more realistic geometries, finite outer potential walls, and better description of the band structure, using real-space methods, multi-band models, and tight-binding Hamiltonians or ‘dressed’ orbitals. Time-difference simulations can be reduced by a factor of 5-10.

Dynamic state selection allows the computer, by generic selection criteria, to use only those determinants that are momentary most important. This approach is especially useful in multi-pulse simulations where the coupled determinants belong to different classes at different times.

Supported by NSF, NCSA and OSC.

9:45 AM B3.4
THE ORIGIN AND NATURE OF STABLE ULTRAVIOLET TO RED LIGHT EMISSION FROM SILICON NANOCRYSTALS.
Howard W.H. Lee, Gildardo Delgado, Lawrence Livermore National Laboratory, Livermore, CA; Peter A. Thelen, University of California at Davis, Dept of Applied Science, Livermore, CA; Susan M. Kranichried, Chang Sung Yang and Daniel Migeri, University of California at Davis, Dept of Chemistry, Davis, CA.

We observe intense and stable size-dependent luminescence from Si nanocrystals that can be continually tuned from the ultraviolet to the red, and we clarify the origin and nature of this light emission. These nanocrystals have surfaces terminated with either silicon oxide or organic alkyl groups. Nanocrystals with different surface terminations exhibit similar optical properties, indicating luminescence from the Si nanocrystalline core. The luminescence mechanism can be separated into quantum confined and non-quantum confined contributions. Monitoring this photoluminescence (PL) produces shifts in the photoluminescence excitation (PLE) spectra that indicate size-dependent energy gaps in agreement with pseudopotential and tight binding calculations for quantum confined Si nanocrystals. Energy levels and spectra of non-quantum confined sources should not depend on the Si core size and should shift in this specific manner. Power dependent PL studies confirm this. Our results show that quantum confinement in Si nanocrystals is largely responsible for the tunable emission. The quantum confined luminescence is surprisingly maintained in indirect character even down to small sizes (<10 nm) as indicated by phonon replicas in resonantly excited PL and by phonon absorption and emission in the PLE spectrum. Size-terminaled nanocrystals also show visible luminescence from non-quantum confined sources such as traps that are defects in the surface oxide layer. This occurs in the red (1.7 - 1.8 eV), green (2.5 eV), and blue-green (2.7 eV). It is size-independent and may be mistaken for quantum confined luminescence. Non-quantum confined mechanisms that give rise to emission below the bandgap are required for the interpretation of visible light emission from nanostructured Si nanocrystals with organically modified metal alkyl groups show only quantum confined luminescence indicating the complete and defect-free nature of the alkyl surface termination. Work at LLNL was performed under the auspices of the US DoE by Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

10:30 AM *B3.5
EXCITATION SPECTRA IN THE TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY WITH GRADIENT CORRECTION.
Nacho Zueco, Santiago Alcubierre, Departamento de Física, Tokyo Institute of Technology, Tokyo, JAPAN.

Although the density-functional theory was originally devised to describe the ground-state physical properties of interacting many-electron systems, the time-dependent density-functional treatment with the local-density approximation has been applied to various systems including atoms, molecules, and clusters during the last two decades, and it is now proven to work in describing the excitation spectra with unexpectedly high accuracy. Therefore, the extension beyond the time-dependent local-density approximation is now of high importance and interest. We apply the time-dependent density-functional theory with the gradient correction in describing asymptotic behavior to K and Na clusters. We use the jellium background model which is known to work quantitatively very well for
alkalimetal clusters. Hence the system is ideal for examining the relative accuracy of the various theoretical methods for excitation spectra. It is known that the collective excitation energies are systematically improved by the inclusion of the gradient correction.

11:00 AM B3.6
A THREE-DIMENSIONAL COMPUTER MODEL IN SIMULATING OF THE LIGHT-TRAPPING EFFECT IN POROUS SILICON. Peter T. Charbel and Jin P. Zheng, Department of Electrical Engineering, Florida A&M University and Florida State University, Tallahassee, FL.

It has been demonstrated that the porous silicon could be used to enhance the sensitivity, spectral bandwidth, and light acceptance angle of photodiodes. In an attempt to better understand and the light trapping effect of porous silicon, a three-dimensional model was used to approximate the surface geometry of the porous silicon. It was found that the main contributing factor leading to such high efficiencies is the shape of the pores. The general shape they take resembles cylindrical or cone shaped sections, whose radii are in the micron range. Although there are several factors that affect the absorption of the incident light, including the wavelength of the light and optical interference, the greatest contribution came from the light trapping shape of the pores. A three-dimensional computer model of a pore was created by using Boolean geometry to remove a conic section from a tetrahedron, where the tetrahedron represents the silicon wafer and the conic section is the pore etched from the surface. By using geometrical optics and ray tracing methods, the efficiency of the modeled pore was obtained by simulating the projection of light onto the surface of the model. The simulation involved obtaining efficiencies for the porous silicon model under different conditions, including variable angles of incidence for the projected light, variable polarization of the projected light, and variable porosity of the silicon. The results of the computer simulation were compared to experimental results where a porous silicon was tested under variable conditions of lighting and porosity. The comparison shows that the simulation gives a good approximation of the behavior of porous silicon. Although the simulation does not perfectly match actual values, it does provide insight into the surface geometry of porous silicon and the main contributing factor to its efficiency in trapping light.

11:15 AM B3.7
HIGH-FREQUENCY DIELECTRIC RESPONSE OF DENSE AND POROUS GLASSES. E. Guibert and J. Kielland, Department of Materials Science and Engineering, University of Illinois, Urbana, IL.

Large-scale molecular dynamic computer simulations have been used to generate amorphous structures exhibiting a range of densities and pore structures. Atomic interaction models used in this study account for charge transfer and the dynamic polarization of larger ions, and are designed to describe network glass formers, such as silicon and boron oxide. The evaluation of the dielectric properties of these systems included assessment of dynamic band to atomic trajectories, as well as the establishment of correlations between meso-scale pore structures and the lower-frequency dielectric response. Finally, an attempt is made to develop continuum representations of these porous structures, which exhibit the same properties as the atomic models.

11:30 AM B3.8

Quantum dots based on GaAs/AlGaAs modulation doped heterostructures have been grown by molecular beam epitaxy in a field effect arrangement. Such field effect devices allow the number of electrons confined in the quantum dots to be tuned electrostatically from 0 to approximately 6 simply by using a gate potential. With such a fine level of tunability, we have been able to study few electron-electron interactions in semiconductor quantum dots. In the present work, the properties of such interacting electrons are probed optically at 4.2 K by measuring the absorption and emission of excitons confined in the dots together with the stored charge. The “transmutation” from Hydrogen-like to Carbon-like quantum dots can be therefore monitored optically while sweeping the gate voltage applied on the dots. Samples were grown with two different type of confinement potentials, namely “ring-like” and “paraboloid-like”. We measured the excitonic emission spectra originating from a single quantum dot as a function of the number of electrons present in it. The energies and the amplitudes of the absorption and emission peaks are found to be directly correlated with the number of charges present in the dots. While the experimental results for the paraboloid-like dots are found to be very well accounted for by an analytical Hartree-Fock perturbation theory in the strong confinement limit, the more novel ring-like quantum dots are presently not fully understood and offer new interesting challenges. [1] R.J. Warburton et al. Phys. Rev. B58, 16 221 (1998).

SESSION B4:
Chair: Gerardo Martinez
Wednesday Afternoon, December 1, 1999
Room 269 (H)

1:30 PM B4.1
OPTICAL ABSORPTION AND INELASTIC LIFETIMES IN NOBLE METALS A. Hulbig, Djao, Pisac Teorica, Valdahol, SPAIN; I. Campbell, J.M. Pitarke, Materia Kondensatoren Pisac Sali, Euskal Herriko Universitatea, Bilbao, SPAIN; E. Zurek, P.M. Echenique, Materia Kondensatoren Pisac Sali, Euskal Herriko Universitatea, San Sebastian, SPAIN.

Applications of the Time Dependent Density Functional Formalism to calculate the response of metallic and semiconducting systems to static and time-dependent electric fields are reviewed. We analyze in detail the role of the localized d bands in the dynamical response of noble metals (Cu, Ag and Au). We also present new data on the inelastic lifetimes of excited electrons computed within the GW approximation. Our fully band-structure calculations indicate that actual lifetimes are the result of a delicate balance between localization, density of states, screening, and Fermi-surface topology. Comparison with experiments is made and discussion for further improvements is outlined.

2:00 PM B4.2
ACTIONS OF ELECTRON-ELECTRON INTERACTION IN MAGNETO-OPTICAL SPECTRA OF 2D SEMICONDUCTOR STRUCTURES. Marek Potemski, Grenoble High Magnetic Field Laboratory, MPI/FRK and CNRS, Grenoble, FRANCE.

In the presence of free carriers, which can be optically excited or of extrinsic origin, electron–electron interactions induce changes in the optical properties of semiconductors. These many-body interactions have been rediscovered an interest in the study of conduction in confined electronic systems such as optically pumped and/or modulation doped quantum well structures. Two-dimensional electronic systems subjected to high magnetic fields are of particular interest, firstly due to the simplified experimental conditions (discrete energy levels) and secondly due to the unique nature of electron-electron interactions in the case of fully degenerate electronic levels (quantum Hall regime). The effects attributed to many-body interactions, observed in interband magneto-optical spectra involving two-dimensional electron gas and electron-hole plasmas will be discussed. Particular attention will be focused to processes of optical recombination from a two-dimensional electron gas under Landau quantization conditions. Apparent discrepancies between experimental observations and theoretical understanding of many-body features in the optical spectra of 2D semiconductors will be outlined.

2:30 PM B4.3
OPTICAL AND TRANSPORT PROPERTIES OF METALS FROM FPPLAW CALCULATION. Kazuo Ushio, John S. Tse. Stacie Institute for Molecular Science, National Research Council of Canada, Ottawa, CANADA.

The optical properties and electronic transport properties of solid are directly related to the topology of the Fermi surface. For example, plasma frequency is calculated from the Fermi velocity, Hall coefficient is calculated from first and second derivatives of the Fermi surface. The evolution of those physical quantities requires accurate bandstructure on very fine k-point grid. The recent development of highly accurate electronic structure calculation method and technique of band fitting procedure enables our exploration of potential of novel materials from first-principles calculation. A full-potential linearized augmented plane wave [APW] method in a framework of density functional theory (DFT) is one of the most accurate electronic structure calculation method and it has been applied many solid state systems such as transition metals, semiconductors and high-Tc superconductors. Because the FPPLAW method is an all-electron method, which involves core electrons explicitly in the calculation, we can obtain X-ray absorption/emission spectra, Knight shift, dielectric tensor, plasma frequency within an accuracy of DFT, we have implemented modified SKW band interpolation scheme to the FPPLAW method and calculated the Fermi surface and its derivatives on very dense k-point grid with small computational cost. We present the detailed analysis of the Fermi surface and results of plasma frequency, Hall coefficient and thermoelectric effect for some metals and alloys.
We present \textit{ab initio} calculations of the optical properties of metallic surfaces. We consider the (110) clean surface of Cu for which the anisotropic surface reflectivity (ASR) has been recently measured [1]. This technique takes advantage of the anisotropy induced by a surface in an otherwise symmetric bulk lattice. With an implemented PP-LMTO code [2], we compute the optical properties, i.e., the dielectric function, and hence the ASR. We use the slab technique, including 11 atomic layers and 4 vacuum layers. The resulting ASR spectrum agrees with the experimental curve. In particular, the large peak at about 2 eV and the structures about 4 and 5 eV found experimentally can be reproduced by the present calculations. Considering a smaller slab of only 7 atomic layers, gives only a qualitative agreement between measured and computed ASR. We also interpret the observed ASR structures through the analysis of interband transitions among the bulklike, surface-like and bulk-surface electronic states. To our knowledge, these are the first \textit{ab initio} calculations of optical properties of metallic surfaces.


3:30 PM • B4.5
DOPANT-INDUCED STRUCTURAL INSTABILITIES AND PERSISTENT-PhotoconDUCTIVITY IN SEMICONDUCTORS AND INSULATORS. D.J. Chadi, NEC Research Institute, Princeton, NJ.

Over the last decade it has become increasingly evident that many dopants commonly used in the p- and n-doping of semiconductors induce a structural instability as an atomic level. The instability is often accompanied by the phenomenon of persistent-photoconductivity (PPC) in which the dopant undergoes a transition from a deep state into a shallow state upon exposure to light. The ability to calculate total energies with high accuracy has led to the identification of the two primary low energy states responsible for PPC. A review of the main results for III-V and II-VI semiconductors and in the very large band gap material CdF$_2$ will be given in this talk.

4:00 PM • B4.6
DEFECT AND PRESSURE INDUCED EFFECTS ON OPTICAL PROPERTIES OF MOLECULAR CRYSTALS. Majid M. Kulkia, A. Barry Kunz, Electrical Engineering Department, Michigan Technological University, Houghton, MI.

Molecular crystals belong to a wide class of the technologically important materials. Most of them are composed of polyatomic molecules having a complicated structure. In the present study, the defect- and surface-induced effects on the optical band gap of a solid CH$_3$NO$_2$ (KNO$_2$, intercalated) are investigated by a first-principles, quantum-chemical method. The Hartree-Fock calculation scheme (CRYSTAL05) combined with the many-body perturbation theory (LAPW) permits us to simulate the atomic and electronic structure of a series of lattice defects in RDX such as a molecular vacancy, a vacancy dimer, an edge dislocation, a nano-crack, and a (210) surface. As a result, we can predict how their presence in the crystal will affect its optical properties. The effect of high external pressure on the electrical and optical properties of the material is also studied. It is well known that some materials lose their transparency under high compression. This phenomenon, for example, is characteristic for detonation initiation in high explosive solids, which undergo an explosive phase transition. In our study, the critical pressure for the insulator-metal phase transition in RDX is predicted and analyzed for both the defect-free material and the solid containing defects. The obtained results compared with the relevant experimental data and are of great practical importance, in particular, our conclusions provide useful insights for the control of sensitivity of explosive crystals to detonation initiation.

4:15 PM • B4.7
FIRST-PRINCIPLES CALCULATIONS OF OPTICAL PROPERTIES OF SURFACES. Cecilia Noguez, Instituto de Fisica, Universidad Nacional Autonoma de Mexico, Mexico DF, MEXICO.

We developed a first-principles method to calculate optical properties of surfaces starting from their fully relaxed atomic configurations. We present a method that employs a localized pseudopotential orbital basis set. This approach deals with inhomogeneous systems, surfaces, consisting of up to several hundred atoms per unit cell. We present results for GaN surfaces, in terms of their calculated optical surface dielectric response function. We compare the results with semipirical tight-binding calculations and experimental measurements.

SESSION B5 POSTER SESSION
Chair: James R. Chelikowsky
Wednesday Evening, December 1, 1999
8:00 P.M. Exhibition Hall D

B5.1 COMPUTATION OF THE POROUS Si DIELECTRIC FUNCTION IN THE SUPERLATTICE MODEL AND COMPARISON WITH EXPERIMENT. Julia Tagueni-Martinez, Yuri Rubo, CIE-UNAM, MEXICO, Miguel Cruz, ESIME-IPN, Mexico City, MEXICO, Marcela Beltran, Chamin Wong, IIM-UNAM, Mexico City, MEXICO.

We present the results for the imaginary part of the dielectric function of porous silicon, which were obtained with the tight-binding 128-atom supercell model [1] for porosities 61%, 70%, and 76%. For the 70% porosity case we have also considered a few different pore morphologies. The onset of the absorption depends substantially on porosity and morphology, which also affect the width of the main absorption peak. In particular, the width increases noticeably for low-symmetry pores. Since the real samples have pores of different sizes and shapes, we have performed a statistical average over these parameters to compare with the experimental data [2]. References: [1] M. Cruz et al., Phys. Rev. B 59 15281 (1999). [2] N. Koshita et al., Appl. Phys. Lett. 63, 2774 (1993).

B5.2 MINIBAND STRUCTURE AND OPTICAL TRANSITIONS IN A SUPERLATTICE WITH ELECTRON QUASI-LOCALIZED STATES IN UNIT CELL. Alexei Dmitriev, Vladimir Makeyev, Moscow State Univ, Dept of Low Temperature Physics, Moscow, RUSSIA.

We studied theoretically the miniband structure and optical transitions in a superlattice with quasi-localized (resonant) electron states in unit cell. We considered the superlattice or multiquantum well structure (MQWS) with unit cell that contains a well, the main barrier separating the welling in the neighboring cells, and two additional semi-transparent barriers at both sides of the well. The additional barriers form resonant electron states at energies above the main barriers.

A dispersion relation and carrier wave functions were found for such superlattices, and their miniband structure was calculated. Near energies of the resonant states the electron spectrum and wave functions have specific hybrid properties where features of under- and above-barrier states are intermixed. The shape of a miniband formed by the quasi-localized states differs significantly from that of minibands consisting of barrier states. The inter miniband dipole matrix element and the corresponding absorption coefficient for the transitions from states of the lowest miniband were calculated. The absorption increases greatly for the transitions to higher states of the same miniband and then the absorption enhancement may cover several minibands. When the superlattice period tends to infinity, our results agree with those obtained by us earlier for a single quantum well with resonant states.

B5.3 DEFECT INDUCED EFFECTS ON MECHANICAL AND DIELECTRIC PROPERTIES OF YTTRIUM ALUMINUM COMPOUNDS. Majid M. Kulkia, Electrical Engineering Department, Michigan Technological University, Houghton, MI; Institute of Chemical Physics, University of Latvia, Riga, LATVIA.

Yttrium Aluminum compounds are important materials, which technolgoical applications range from lasers to propulsion systems. For example, the Nd$^3+$ doped YAG is a wellknown laser material whereas YAG:Al$_2$O$_3$ composite is found to be an ideal material for high-temperature ceramic applications. In the present study, theoretical simulations of mechanical and dielectric properties depending on basic point defects in Yttrium-Aluminum Compounds such as Porsekite (YAlO$_3$) and Garnet (Y$_3$Al$_5$O$_{12}$) crystals were performed in terms of interatomic potentials coupled with the classical shell model description of the lattice ions. A new set of potential parameters first obtained for the perfect lattice allows us to model atomic structures of different types of the intrinsic (vacancies, interstitials, antisites) and impurities (Cu$^{+4}$, Mg$^{2+}$, Ba$^{2+}$, Si$^{4+}$, Fe$^{3+}$, Nd$^{3+}$, S$^{4+}$) point defects. Using the calculated defect formation energies we obtain activation energies for defect reactions, from which we determine the most probable defect processes in Yttrium-Aluminum porosekite and garnet. We found that both
compounds the intrinsic disorder is more favorable than the Penzel and Schottky-like disorder. It is shown that intrinsic substitution YAl creates a distorsion crystalline lattice bond length whose calculated value is in excellent agreement with the EXAFS measurements. Deviations from stoichiometry were modeled by an excess of yttrium and aluminum oxides. Some other properties such as effective mass, density of states, and optical absorption in elastic properties, and complex defect cluster formations as well as migration mechanisms were also considered. A comparison with the relevant experimental data is presented.

B5.4 HIGHLY REFLECTIVE MIRRORS FOR DER APPLICATIONS OPERATING B5.5 At. 510 G0.3 AlGaAs/InP MATERIAL SYSTEMS Lennk. A. Christou Materials and M. Nuclear Engineering Department, University of Maryland at College Park, MD.

Theoretical optimization of the refractive indices and energy band gaps of the III-V quantum wells in the form $A_{x}B_{y}C_{1-x-y}D_{y}$, and $A_{x}B_{y}C_{1-x-y}D_{y}$ was conducted as a function of the incident wavelength and the alloy composition. The investigation and comparison of the refractive indices of the quantum wells lattice matched to InP revealed two highly reflective material systems, $G_{0.3}A_{0.7}B_{0.6}C_{0.13}D_{0.07}$ and $G_{0.3}A_{0.7}B_{0.6}D_{0.13}C_{0.07}$ which may be used as distributed Bragg reflectors lasing at 1.55 μm due to the large optical index difference they provide between alternating layers. A reflectivity of 99% can be achieved by growing only 15 pairs of AlGaAs/InP or GaInAs/InP Bragg mirrors on InP substrate and taking GaInAs as an active layer.

B5.5 ELECTRONIC STATES OF SELF-ASSEMBLED QUANTUM DOTS WITH LENS GEOMETRY THE ROLE OF SYMMETRIES. C. Trailer-Gómez, A. Hernández-Rodríguez, J. Martín-Antúñes, Department of Theoretical Physics, University of Havana, CUBA, E. Urion. Department of Physics and Astronomy, Ohio University, Athens, OH.

Self-assembled semiconductor quantum dots are modeled with a geometry of lens shape described by a spherical cap of height b and circular cross section with radius a. In an envelope function formalism, the corresponding Hamiltonian for a carrier confined in this lens geometry is mapped into an equivalent equation with semi-spherical shape. Geometrical effects on carriers energies and wavefunctions as a function of the lens height b are studied. Exact solutions are reported for the particular case of b = a and a modified Rayleigh-Schrödinger perturbation theory is applied to obtain analytical expressions for the energy levels and eigenfunctions, as function of the b/a ratio. Numerical calculations are presented for confinement by an infinite hard wall. The degeneracy due to the z-component of the angular moment m is broken for b = a. Energetic states with m = 0 present the most pronounced influence on b = a. The band width is observed for the eigenfunctions of the quantum dot with lens-shape symmetry. The effect of decreasing symmetry on the excition binding energy is studied also using a numerical method diagonalization in terms of the obtained electron and hole wavefunctions as basis set. Analytical expressions presented here can be used to estimate the sizes of natural self-assembled quantum dots. Finally, we present the role that these states play on the excitonic states and optical response of such quantum dots.

B5.6 LOCAL BASIS GW CALCULATIONS AND THE DIELECTRIC RESPONSE OF SILICON CLUSTERS. Ming Yu, Yung Ie. Ullom and David A. Drabold, Department of Physics and Astronomy and Condensed Matter and Surface Science Program, Ohio University, Athens, OH.

We present our progress in developing an ab initio computational scheme for calculation of the dielectric response function of solids, with special emphasis here in Si clusters. All calculations are carried out employing a basis of localized atomic-like orbitals and include the evaluation of quasiparticle corrections. The self-energy operator is evaluated in the GW approximation, with a full frequency dependence for the dielectric matrix. The approach is convenient and computationally optimal for the calculation of optical properties of complex systems lacking periodicity, such as surfaces and clusters. We present here the quasiparticle energy structure for Si20 and Si50 clusters with structures found from full equilibration via molecular dynamics simulations. We also discuss the degree of nonlocality of quasiparticle properties to quasiparticle corrections, and the convergence with respect to the size of the localized orbital basis. Comparisons are also made with bulk silicon calculations in the generalized pole approximation. We find that the optical gap in clusters larger than in bulk silicon, likely the result of size quantization and structural disorder.

B5.7 INTERACTION OF MOLECULES WITH ULTRA-SHORT INTENSE LASER PULSES A NONADIABATIC QUANTUM MOLECULAR DYNAMICS APPROACH. Thomas Niehaus, German Cancer Research Center, Dept. of Molecular Biophysics, Heidelberg, GERMANY; Ben Torralba, Dept. of Physics, Texas A&M Univ, College Station, TX; Markus Elsner, Thomas Frauenheim, University of GH Paderborn, Fachbereich Physik, Theoretische Physik, Paderborn, GERMANY; Sandor Suhai, German Cancer Research Center, Dept. of Molecular Biophysics, Heidelberg, GERMANY.

We present a nonadiabatic quantum molecular dynamics approach, which is suitable to study the response of large polyatomic systems to intense laser pulses. Starting from a quantum-classical Lagrangean, coupled equations of motion for electrons and ions are derived. The electronic wavefunction is propagated according to the Kohn-Sham equation of time dependent density functional theory. We implemented this scheme using a density functional based tight-binding method [1], where the necessary matrices are determined within a confined LCAO basis in a two-center representation. Forces on the nuclei are obtained from a generalised Ehrenfest theorem and the external radiation field is incorporated via minimal coupling, where following Graf and Vogl [2] the field dependent matrices may be rewritten in a numerical feasible way. Results show the dominant photoexcitation of the breathing mode in Cs and the red-shift of this mode due to ultra-intense laser pulses with fluences on the order of 4.0 kJ/m². These findings agree well with pump-probe experiments on thin films recorded by Doehner et al. [3].

B5.8 OPTIMIZED PROPERTIES OF SEMICONDUCTORS USING DENSITY FUNCTIONAL THEORY. S.J. Clark and R.A. Abram, The University of Durham, Department of Physics, Science Labs, Durham, UNITED KINGDOM.

The need to make reliable simulation of optical properties of materials is becoming increasingly important and new techniques make demands for highly specialized semiconducting devices. One of the most commonly used first principles methods for calculating electronic, and therefore optical properties of materials is density functional theory. However, the major drawback of this method is that it underestimates the band gap of materials, often by up to 50%, which can be traced back to the single particle excited state Kohn-Sham orbitals and the need for a discontinuity in the exchange-correlation functional, which is not correctly described by the usual local density functional generalised gradient approximations. This leads to a poor description of excited state energies which appears as an underestimation in the electronic band gap. We have performed band structure calculations on a range of semiconducting and insulating materials using a constrained excited state energy technique, combined with an exchange-correlation functional within the generalised gradient approximation which corrects for long-ranged correlation effects. This combined technique predicts band gaps within a few percent of experimental values without any additional computational cost.

B5.9 OPTICAL AND DIELECTRIC PROPERTIES OF AlGaIn S0LID ALLOY. Ivan Kryk, Michal J. Młodawski, Pedagogical Univ., Institute of Physics, Cracow, POLAND.

Calculated results for band structure of AlGaIn solid alloy are shown. We present the solid alloy structure as a superposition of two sublattices with the appropriate weighting factors. Both the ab initio norm-conserving pseudo-potential (PP) and LCAO methods give essential disagreement with the experimental data. Only the appropriate correction of the norm-conserving PP method by the orthogonalized LCAO wave functions essentially outlines the correct procedure. To check the reliability of the presented method we have carried out experimental investigation of the optical functions for two representatives of the investigated wurtzite AlGaIn solid alloys. Calculations were performed as a function of energy current with orthogonalization of the norm-conserving pseudowave function to the LCAO wavefunctions. The optical functions at zero frequency give an overestimated values comparing with the experimental data. The best agreement with the experimental can be achieved by using the norm-conserving pseudowave and LCAO wavefunctions. The last ones help in understanding of the appearance of the solid alloy structure.
modulations in the mentioned compounds. The spectral dependence of absorption coefficients for \( \text{GaN} \) and \( \text{AlGaN} \) are of crucial importance. So-called quantum size effect is commonly used in spite of some discrepancies with the available experimental data. The results of our calculation concerning the band structure enabled realization a numerical evaluation of spectral dependence of absorption coefficient. The results were compared with the square root law as well as with the experimental data available in the literature.

**B5.10**

**COMPUTATION OF OPTICAL PROPERTIES FOR QUANTIZED ELECTRONIC SYSTEMS**

Verne I. Jacobs, Center for Computational Materials Science, Materials Science and Technology Division, Naval Research Laboratory, Washington, D.C.

A density-matrix description has been developed to treat relaxation (decoherence) phenomena during resonant and non-resonant radiative transitions of quantized electronic systems, including many-electron atoms and quantum confinement systems (e.g., semiconductor microstructures). Radiative and collisional relaxation phenomena have been treated using Liouville-space projection-operator techniques. Both time-independent (resonant-operator) and time-dependent (equation-of-motion) formulations have been developed. The self-energy operators that occur in these formulations can provide the fundamental basis for a self-consistent determination of the non-equilibrium and coherent electron wave kinetic equations together with the homogeneous spectral-line shapes. This density-matrix description can be adapted for the computer simulation of electromagnetic processes. From first-principles electronic-structure calculations or from semiempirical approaches, the parameters describing the elementary collisional and radiative interactions can be evaluated and organized into the basic dataset for the application of density-matrix description. The final product is a theoretical prediction for the linear or non-linear optical absorption or emission spectrum corresponding to a given set of values for the appropriate physical variables, such as temperatures, densities, and electric or magnetic field strengths. This work has been supported by the Department of Energy and by the Office of Naval Research.

**B5.11**

**FIRST-PRINCIPLES CALCULATION OF OPTICAL SPECTRA FOR \( \text{Cr}^{3+} \) DOPED IN \( \text{Al}_2\text{O}_3 \) AND \( \text{MgO} \)**

Kunioyuki Ogawa, Matsunobu Yurumori, Takahiro Ishii, Teruyasu Mihashita, Fumiyasu Ohno, Hirohiko Aida, Kyoto University, Dept. of Materials Science and Engineering, Sakyo-ku, Kyoto, Japan

The multiple structures of \( \text{Cr}^{3+} \) doped in \( \text{Al}_2\text{O}_3 \) (\( \alpha \)-\( \text{Al}_2\text{O}_3 \), \( \text{Cr}^{3+} \) and \( \text{MgO} \) \( \text{Cr}^{3+} \) are calculated from first-principles using a hybridized method of the density functional theory (DFT) and the configuration interaction (CI) approximation (DFT-CI approach). In the DFT-CI approach, the single-electron orbitals are calculated by a spin-restricted density functional calculation. Then the many-electron wave functions are expressed as linear combination of Slater determinants by diagonalizing the many-electron Hamiltonian. The reduction of electron-electron repulsion integrals due to electron correlation is evaluated from the consistency between the spin-unrestricted density functional calculation and the DFT-CI calculation. The structural relaxations around the impurity \( \text{Cr}^{3+} \) ions are also taken into account by static energy minimization technique using pair potentials. In the case of \( \text{Al}_2\text{O}_3 \) and \( \text{MgO} \), the intensity of the electronic transition arising from the non-rigid ion distortion are calculated numerically using the many-electron wave functions obtained by the DFT-CI calculation. The calculated intensity qualitatively reproduces the similarity of the absorption spectra of ruby. In the case of \( \text{MgO} \), there are \( \text{Mg}^{2+} \) vacancy for every two \( \text{Cr}^{3+} \) in order to satisfy the charge neutrality and there are slightly distorted sites with tetragonal or rhombohedral symmetry according to the position of the \( \text{Mg}^{2+} \) vacancy. The intensity of the electronic-dipole transition arising from the non-rigid ion distortion are calculated by using the simple computational approach and are compared with the absorption spectra of \( \text{MgO} \) \( \text{Cr}^{3+} \).

**B5.12**

**THEORETICAL INVESTIGATION OF THE GEOMETRICAL AND ELECTRONIC STRUCTURES AND NONLINEAR OPTICAL HYPERPOLARIZABILITIES OF SOME FUSED HETEROCYCLIC AROMATIC COMPOUNDS**

Michael M. Baldwin, Dep. of Chemistry, Penn State University, Hazleton, PA.

Results of our ab initio calculations of the geometrical and electronic structures and the SHG hyperpolarizabilities of a series of heterocyclic aromatic molecules [based on pyridine] containing different donor and acceptor groups will be presented. 15 compounds are considered in this study. The effect of geometry, type and relative positions of the substituents on the molecular properties will be discussed. The set dependence of the calculated parameters will also be addressed.

**B5.13**

**PLASMON REFLECTION OF LIGHT BY CRYSTALS IN THE FRAME OF THREE-LAYER MODEL**

P. Kosoboski, T. Slynukha, A. Danilov, State University Lviv Polytechnic, Dept. of Physics, Lviv, UKRAINE.

The theoretical study of conditional of extremum in plasmon reflection spectra for crystals with non-dispersive layer on surface is carried out. It was determined that minimum of reflection contour \( R_{\omega}(\omega) \) forms at frequency \( \omega_\text{m} \) when wave phase shift in the layer and for reflection from internal layer-substrate interboundary equals \( \varphi_{\omega,\delta} = 2\pi \), where \( \delta = 4\pi l / \lambda \) is wave phase shift in the layer with thickness \( d \) and index of refraction \( n \), from the condition of phase compensation for three-layer model we obtained the relation between \( \omega_\text{m} \), \( \delta \), and optical indices of refraction and absorption of electromagnetic wave in substrate volume:

\[
\omega_m^2 \approx \frac{\omega_0^2}{\omega_0^2 - \frac{1}{2} \left( \omega_0^2 - \omega_0^2 \right)}
\]

where \( \omega_0 \) is the plasmonic frequency, \( \epsilon_\text{e} \) is the dielectric constant with nonresonant contribution of bound charge. For the case we assume, that dumping factor \( \gamma = 0 \). As was determined, extremum position strongly depend on both angle of incidence and phase thickness of the layer on surface. The shape of plasmon spectrum near resonant region is investigated. If the hodograph of complex reflection coefficient \( r \) passes through origin of coordinate axes \( Re r_1, 0 \) the phase spectrum changes of \( S \rightarrow N \) type take place.

**B5.14**

**THE INFLUENCE OF 5 AND 6 ATOM RINGS ON THE OPTICAL PROPERTIES OF a-SILICON NITRIDE: A CLUSTER SIMULATION**

R.M. Valladares, A.G. Calles, Facultad de Ciencias, UNAM, Mexico, DF., MEXICO; Alexander Vallades, Ariel A. Valladas, Instituto de Investigaciones en Materiales, UNAM, Mexico, DF., MEXICO.

We simulate \( a - \text{SiN} \) with two types of clusters: \( a - \text{Si}_{25}\text{N}_{13} \); \( H \) that contains 6 atom bond-type rings and \( a - \text{Si}_{25}\text{N}_{13} \); \( H \) that contains 5 atom plane rings, where \( i = 0, 1, 2, 3 \). The simulations were carried out using the DFT-LDA approximation contained in the DMol code of MSI. We report calculations of impurity levels and relate these to the size of the gap and to the optical absorption curves for each cluster. A comparison is made between the two \( a - \text{SiN} \) clusters studied to analyze the effect of the ring topology as well as to experiment. Clusters are useful to investigate the influence of specific structures or defects in amorphous materials. [1] Optical Properties of Tetrahedral a-Carbon Nitride, A.A. Valladas et al. To be published in Synth. Metals. [2] Influence of 5 atom Rings on the Optical Properties of a-Carbon Nitride, R.M. Valladates et al. To be published in Synth. Metals.

**B5.15**

**SIMULATION OF X-RAY DIFFRACTION ON MULTILAYERS SUBJECTED TO DIFFUSION**

A. Fedory, Institute for Single Crystals, Condensed Molecular Films Division, Kharkov, UKRAINE.

Multilayers with great difference of electron density of alternating layers widely used in X-ray optics as dispersing elements, or X-ray mirrors. Their efficiency depends among others from interlayer diffusion, which may lead to abruptness and flatness and from stability under heavy radiation and temperature influence. The diffusion intermixing and formation of new phases on the boundaries may take place in these circumstances. Mathematical description of low angle X-ray diffraction on these structures and resulting diffraction pattern is commonly based on Fresnel equations, that supposes the presence of uniform dielectric constant by the layer and abrupt interfaces. But real multilayer may not offer such ideal rect angular profile. Usually, the way out is to approximate such smooth profile as a set of lamellae. In this work another approach is considered based on solution of Maxwell equations for layered structure with arbitrary profile of dielectric constant distribution. Solution gives the Riccati type equation for angular dependence of reflectivity \( R \) in X-ray wave range

\[
\frac{dR}{d\delta} = -2\kappa R \left[ 4 \sin \varphi \right] \left[ 1 + R^2 \right] \sin \varphi = \left[ \frac{1}{4 \sin \varphi} \right] \left[ \frac{1}{4 \sin \varphi} \right]
\]

where \( e^2 \) is the electric constant \( e^2 \) in X-ray wave range defined as \( e^2 = 1 - \delta \), \( \delta = \frac{\rho}{\rho_0} \cdot \delta \), \( \rho_0 \) is the electric constant \( \rho_0 \) in X-ray wave range and \( \rho_0 = \frac{1}{4 \sin \varphi} \).

\[
\frac{dR}{d\delta} = -2\kappa R \left[ 4 \sin \varphi \right] \left[ \frac{1}{4 \sin \varphi} \right]
\]

\[
\lambda^2 = \frac{\rho}{\rho_0} \cdot \delta^2 + \frac{1}{4 \sin \varphi} \cdot \delta^2
\]
and

\[ R = R_0 \exp(-2 \sqrt{\frac{\hbar k}{\varepsilon}} \sin^{-\frac{1}{2}} \varphi) \]  

(2)

where \( \varphi \) - film thickness, initial condition \( R_0 \) is the known Fresnel equation for reflection from the boundary of two media. This is just the equation (2) the present method was found to provide a simple case of a rectangular multilayer profile. Using (1) solved numerically with Runge-Kutta 4th order method the X-ray diffraction patterns were calculated for different conditions of profile transformations. It was shown that with different coefficients on the neighboring boundaries that leads to asymmetrical profile transformation causes reduction of some reflections and increase of other ones.

B.5.16 ENERGY DISPERSION CONTOUR APPROACH TO CALCULATE OPTICAL PROPERTIES OF QUANTUM WELL STRUCTURES. T. Otschach, C. Wu, S. Zhang, School of Electrical and Electronic Engineering, Nanyang Technological University, SINGAPORE.

In order to calculate optical properties i.e. dielectric function, refractive index and absorption coefficient, the evaluation of integration including ground and excited wavefunctions is required over entire k-space. The contour of energy dispersion was proposed to form the criteria to select and limit the value of \( k \) in the integration. With the contour approach the integration can be determined to truncates at certain \( k \) value where the weight factor of Fermi-Dirac distribution function become very small and the fraction of integration can be ignored. The approach was applied to AlGaAs/AlAs/GaAs double barrier quantum well structures with 14-band kp Hamiltonian. By systematically modify this quantum well structure the dependence of absorption peak width was investigated in bound-ordered bound and bound-ordered interband transitions. The energy dispersion contours of each involved state were illustrated in two dimensional k-space with the compositions in perpendicular and parallel directions to the interface. 

The calculated refractive index and absorption as a function of wavelength can be simply extracted from the contour characteristic especially at the constant Fermi energy surface.


Si K\(\alpha\) X-ray emission spectra of SiO\(_2\)/CaO binary glasses simulated by the DV-X\(a\) molecular orbital calculation were compared with compositions measured by EMPA. The composition of the slag has been incorporated in the calculation of the partial density of states of 3p component of Si ion. The calculated partial density of states of 3p component of Si ion as a function of the CaO content agreed well with the measured Si K\(\alpha\) X-ray emission spectra of 62.4mol\%SiO\(_2\), 37.6mol\%CaO and 43.2mol\%SiO\(_2\), 56.7mol\%CaO binary glasses. The present method was found to be a very useful means of clarifying the change in ionic configuration of the glass with the metal oxide content, and also of understanding the concept of basicity at the same time.


The photo-convertible Low Temperature Co-fired Ceramic Tapes is a versatile material system with great potential in the field of micro-scale (where features range from 1 micrometers to several centimeters), 3-D structures, and the packaging of silicon based MEMS. This alumina based glass-ceramic composite system is similar to the conventional LTCC tapers, except that the organic part of the binder composition includes a photo-polymer acting as a resist. This allows the transferring of arbitrary patterns to the tape by use of the nominal tools of UV lithography. The resolution limit seems to be imposed by the diffusive nature of the light scattering within the filler alumina grains. Diffuse light scattering is a random walk phenomenon. The processing consequence of this phenomenon is the enhanced spreading of the mask diffused light in the dimension normal to the light beam, and the subsequent undercutting upon development. We have simulated the diffuse light scattering of UV light in a photo-formable tape. We calculated the form factor \( P(q) \) and the geometry function \( G(q) \) approximated using Mie scattering and \( S(q) \) using the Percus-Yevick hard-sphere potential approximation. With the knowledge of these parameters, we numerically integrated the light diffusion equation with an extended source using Green's function method and experimentally measured the transport mean free path (random walk step) between scattering events. After processing the tape we have achieved features size of 70 microns in a 150 micron - thick tape. We are able to predict well the control of the undercuts due to scattering of the light by alumina grains. The experimental verification of the model utilizes a modified version of diffuse Transmission Spectroscopy (DTS) using the material development characteristics as a sensor. The technique involves the measurement of extinction coefficient by measuring the sample thickness as a function of energy.

B.5.19 FINITE ELEMENT ANALYSIS OF 2-D DIELECTRIC WAVEGUIDES WITH HELMHOLTZ VECTOR EQUATIONS AND VIRTUAL EXTERIOR ELEMENTS. Teyta Zheng, The GWW School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA; NaiKong Bao, Kin-Seng Chiang, Po-Shen Chang, Department of Electronic Engineering, City University of Hong Kong, Kowloon, HONG KONG.

In optical devices, the vector analysis is necessary when the weak guide assumption is invalid. Since what are concerned in an optical field are its electrical field components, it is expected to get the electrical field directly in the analysis in order to achieve more precise electrical field result than looking for the magnetic field first then deriving the electrical field from the magnetic field.

A finite-element-method formulation is developed on the base of the Helmholtz vector equations in terms of transverse electrical field components to characterize two-dimensional dielectric waveguides with arbitrary continuous permittivity profile. Since the dielectric waveguides analysis is sensitive to its boundary conditions, virtual exterior element introduction technique is used to treat continuous permittivity profile. The characteristic finite element analysis to process the remote boundary condition. This technique increases both the computational efficiency and accuracy than introducing a large amount of real finite elements for the remote boundary conditions. The propagation constants and cutoff frequencies can be calculated from the resulting eigenvalues, the modal electrical field can be obtained directly from the resulting eigenvectors without any spurious solutions. Numerical results of optical fibers with the parasitic permittivity profile are presented to show the validity of this technique.

B.5.20 FIBER BRAGG GRATINGS GROWTH SIMULATION USING AN INVERSE SCATTERING MATRIX APPROACH. Alessio Manca, Dept of Physics, Cagliari, ITALY.

Fiber Bragg gratings are playing an important role in the field of optical telecommunications and sensors. We have simulated the growth of such gratings, longitudinally written in the core of germanium-doped optical fibers by an Argon ion laser. Following a Koehler-Kroger model, the obtained results are presented. The effect of the chiral nature of the chiral nature of the fiber core is in the geometric and the inefficient band (~240 nm) is considered to be responsible for the effective fiber sensitivity and a two photon absorption process models the dynamics of the refractive index variation. The spatial propagation of light through the grating is described by the coupled wave theory and is calculated by using the inverse scattering matrix technique. The predicted physical properties, the refractivity of gratings and the temporal dispersion of propagating light as a function of wavelength and input power, show that a sustained growth is possible. The scattering matrix approach has proven a useful mean even in the case of temporal evolution with respect to previous works.

B.5.21 EFFECTIVE PERMUTIVITY OF COMPOSITE COMPOSITES. Christin Brouzen, Université de Bretagne Occidentale, FRANCE; A. Bousid, École Centrale de Lyon, FRANCE.

The effective electromagnetic, thermal and mechanical properties of heterogeneous media are commonly related to composition. Composite materials are entities that are important in physics and engineering and are a class of compounds actively investigated for their dielectric properties. Such systems consist of composite inclusions of multicomponent materials embedded in a matrix of a distinct host material. The effects of volume fraction, permittivity, thickness, and shape of the various components on the complex permittivity of the heterostructures are reported. We present calculations of the complex effective permittivity for different types of composite composites, in the quasi-static approximation. We use an exact numerical technique for the evaluation of the dielectric properties of the composite materials, arranged in a regular simple cubic lattice, which is based on the field calculation package PHOENIX and the resolution of boundary integral equations. All internal electric multiple point interactions contributing to the sharp inhomogeneities are neglected. The partials of the effective permittivity, at the critical point where the inclusions
touch, are taken into account. The predictions of Maxwell Garnett (dipolar) theory and the effective medium approximation are in poor agreement with numerical results. Typical results presented for stratified spheres and ellipsoids indicate that any approach based solely on the dipole approximation must fail to predict the effective permittivity of dielectric heterostructures. The results discussed give motivation for the development of careful experiments which can be used to test the numerical simulations and the processing of synthetic composite materials in which new electromagnetic properties can be obtained from the combination of several materials.

SESSION B6
Chair: Marvin F. Cohen
Thursday Morning, December 2, 1999
Room 209 (H)

8:30 AM *B6.1
INELASTIC X-RAY SCATTERING WITH HIGH ENERGY RESOLUTION: A NEW METHOD TO STUDY THE HIGH FREQUENCY ATOM DYNAMICS IN CONDENSED MATTER.
François Seite, European Synchrotron Radiation Facility, Grenoble, France.

One motivation to develop a large and collimated synchrotron sources is the interest to exploit inelastic x-ray scattering as a novel spectroscopic probe for condensed matter. Important limitations imposed by energy resolution requirements, incident and scattered photon energy tunabilities, and photon flux have so far slowed down the development of this technique, and sometimes even questioned its technical feasibility. Only very recently, thanks to the construction of a new ultrastable ring with unprecedented low emittance at the European Synchrotron Radiation Facility in Grenoble, and thanks to new developments of highly performing perfect crystal optics, the scenario is rapidly changing to the point that it is now possible to perform inelastic x-ray scattering measurements in the ~20 keV x-ray energy region with energy resolutions tunable at 7.1, 5 meV.

An important domain of application of the x-ray technique is the study of the high frequency dynamics in the time and length scales domains characteristic of inter-particle density fluctuations. This is traditionally the domain of application of neutron inelastic scattering. When one considers systems without translational invariance, however, the neutron techniques become quite difficult and sometime impossible to use as a consequence of kinematical limitations in the relevant momentum and frequency region. This explains why there are very few coherent inelastic neutron scattering studies on disordered systems, and why there are still many open questions on the high frequency dynamics of liquids, glasses and dense fluids in general. These kinematical limitations are overcome using x-rays. Similarly, the small dimensions of the x-ray beam favour experiments on small sample, eventually in extreme thermodynamic conditions at high pressure.

The present contribution will give an overview on the x-ray inelastic scattering techniques to study of inter-particles dynamics, and it will present some of the results obtained so far on the new instrument, operating in Grenoble since the last five years.

9:00 AM *B6.2
SCREENED EXCHANGE LDA METHODS FOR BULK, FILMS AND SUPERLATTICEs. R. Asaki, W. Marusak and A.J. Freeman, Department of Physics and Astronomy, Northwestern University, Evanston, IL.

We have developed new screened-exchange LDA (s-LDA) methods for films and superlattices (FLM/S) in order to calculate self-consistent electronic structure for both occupied and unoccupied states without adjustable parameters. Considering non-uniform charge densities and local-field effects in the z direction for FLM/S, we employed nonlocal s-LDA to define the screened exchange interaction. Three methods, for bulk, superlattice, and film, are implemented in the full-potential linearized augmented plane wave (FLAPW) method. For bulk Si, Ge, InSb and GaSb, we have presented results of the electronic structures and optical properties obtained with self-consistent eigenfunctions [Phys. Rev. B 50 7268 (1999)]. The results for wurtzite GaN, as a test case, showed that the superlattice method gives us accurate a band structure (including the band gap) and the binding energy of the semiconductor as the bulk one, and that both methods yield identical band structure in the limit of a uniform density used as input to the dielectric function. We have also estimated the film method results of a single Si monolayer slab with those of a superlattice treated as a superlattice including vacuum region. The methods demonstrated here have a wide range of applicability, including possible direct determinations of the band offsets at both conduction and valence bands, and of the Schottky barrier formed by adsorbed metal layers.

Supported by the NSF (through the NU Materials Research Center) and Toyota Central R&D Laboratories, Inc.

9:30 AM B6.3

We demonstrate that the description of the optical reflectance anisotropy of GaAs (110) requires a complete microscopic treatment of both surface and bulk, which is feasible in the discrete cellular model. This method is an extension of standard discrete configuration interaction calculations and accounts for nonlocality in the electromagnetic and quantummechanical interactions through the use of both real space local fields and ab initio nonlocal polarizabilities. The nonlocal polarizabilities are obtained from the ab initio full potential total energy LDA-BAND package. The discrete dipole part of the calculation requires more normal modes then the usual Fresnel ones, to represent the bulk. The results are in excellent agreement with experiment and we show that the anisotropy is surface induced.

9:45 AM B6.4
SEMMEMPERIAL SELF CONSISTENT FIELD MODELING OF THE CeH+4 4f5d5 Energy Levels in Solid State LUMINESCENT MATERIALS. Philip D. Rack, Rochester Institute of Technology, Department of Microelectronic Engineering, Rochester, NY; Ted A. O'Brien, Michael C. Zern, University of Florida, Quantum Theory Project, Gainesville, FL; Paul H. Badger, University of Florida, Department of Materials Science and Engineering, Gainesville, FL.

Rare-earth doped semiconductors are known to be efficient luminescent materials. In particular, SrS and SrCa2–2-xGaxS4 doped with Ce4+ have recently been explored as efficient blue cadmium-doped and electron-luminescent materials for flat panel display applications. The blue emission in these materials is due to Ce4+ 5d-4f transitions, and the transition energies are sensitive to the local chemistry of the Ce4+. To understand the effect that the local chemistry has on the Ce4+ 4f5d emission spectrum, we used a semiempirical self-consistent-field configuration interaction (SCF/CI) model to calculate the electronic spectrum of the Ce4+ ion embedded in a cluster representation of the semiconductor lattice. The effects of changing nearest neighbor ions and cations have been modeled and are in excellent agreement with the experimental spectroscopy. In this presentation we will discuss the SCF/CI model and the cluster geometry used to represent the solid lattice. In addition, we will compare the calculated and experimental Ce4+ 4f5d emission spectra for different materials, and correlate the spectral changes to an analysis of atomic orbital electron populations.

10:00 AM B6.5
THEORETICAL AND EXPERIMENTAL ANALYSIS OF THE LOWER DIELECTRIC CONSTANT OF FLUORINATED SILICA. Alex Demkov, Rui Liu, Stefan Zollner, Dennis Werho, Mike Kotte, Rich Gregory, Semiconductor Product Sector, Motorola, Inc., Mesa, A.M. Asay, Semiconductor Product Sector, Motorola, Inc., Austin, TX, L.C. McIntyre Jr., M.D. Ashbaugh Department of Physics, University of Arizona, Tucson, AZ.

The fluorinated silicas (FTEOS) is known to have the dielectric constant in the range of 3 to 3.5 that is significantly lower than that of the fluorine free material (4). The reasons behind the reduction of the dielectric constant are not very well understood and are somewhat controversial. It is not known whether the electronic or ionic contributions to the overall screening is being diminished upon the fluorine doping. To shed more light on this phenomenon we have studied FTEOS both theoretically with ab-initio modeling and experimentally with various characterization techniques. Pulsed light transmission and spectroscopic ellipsometry measurements gave us the electronic and ionic contributions to the susceptibility. Nuclear reaction analysis was used to measure fluorine composition. XPS and Auger experiments provided the information on the atomic structure of the film. We use a large cell of crystallite to model fluorinated silica theoretically. The ground state geometry is obtained via the energy minimization. Two types of Fluorine have been found; a bridging fluorine acts just as a bridge and forms two Si-F bonds (0.159 nm, and 0.162 nm). In addition, we find a terminal fluorine atom that forms only one bond to Si (0.152 nm). As a result a nano-pore forms in the simulation cell. Analysis of the Si-O-Si bond distribution in the cell shows that even though the Si-O-Si angle of 147° is still very similar to that in fluorine free cristabolite angles as low as 120° and as high as 170° are introduced to the system. We calculate the vibrational density of states at the Gamma point, and analyzed the modes using the inverse participation ratio.
[IPR] IPR indicates localized modes. We find a strongly localized mode at 935 cm⁻¹, this vibration involves the terminal fluorine. The calculations freeze well with the 938 cm⁻¹ vibration excited by far-IR transmission, and with the Si-F stretch reported in the literature. [1, 2] The Auger experiments indicate that mobile F species leaves the molecule if the Al in p is removed. We suggest that it is the terminal fluorine that is mobile. This suggestion is confirmed by the reduction of the 938 cm⁻¹ mode. We compute the electronic and the ionic susceptibilities for models with various fluorine concentrations. The effect of fluorination on the dielectric constant will be discussed. [1] E. Kim, D. R. Nagpure, and G. S. Lee, J. Vac. Sci. Technol. A10, 1509 (1992).


10:45 AM 6D.6 PREDICTING NONLINEAR OPTICAL PROPERTIES OF DELOCALIZED CHARGE STATES IN POLYNYC CHROMOPHORES AND DENDRIMERS. Carl Diet, University of Texas at Austin, Department of Chemistry, and Reza Chai, Emad Hafiz, Emad Hafiz, Lusif Madrini, Montana State University, Dept. of Chemistry and Biochemistry, Optical Technology Center, Bozeman, MT.

While there have been numerous approaches to calculation and prediction of optical properties of organic nonlinear (NLO) optical chromophores, most have focused on linear quasi-1D conjugated chromophores. Thus electron delocalization is confined to the linear chain backbone. Recently, we have utilized a new calculation approach at the Ab-initio level to predicting the optical properties of polyanion radical-cations and bipolaronic diions formed from neutral polyenes with various mesogenically interactive substituent groups. The order of magnitude of the calculated second hyperpolarizability, gamma, and the stabilization ordering by the substituents compare very favorably with experimental results. We have now extended this approach to predicting charge delocalization and stabilization in quasi-1D and -3D dendrimer structures. As the progression from 1d to 3d structures is examined, extremely large enhancements of the bipolaronic gamma is predicted, to the extent that these new materials may be the most nonlinear organic materials yet envisioned. Recent experimental evidence from two-photon absorption measurements on these dendrimers suggest that this prediction may indeed be correct. We thus create new paradigms for the design of third-order NLO materials.

11:00 AM 6F.7 POLYMERIZING CARBON DIOXIDE. Chong-Shik Yoo, Lawrence Livermore National Laboratory, Livermore, CA.

Application of high-pressure strongly perturbs chemical bonds, electronic and crystal structures, thermal and mechanical properties, and reactivities of solids. These pressure-induced changes, however, often occur in systematic ways, providing new routes for designing and synthesizing novel materials with advanced optical and mechanical properties. As an example we report the pressure-induced transition of carbon dioxide from a molecular phase to a novel extended polymeric phase that can be viewed as being similar to its heavier periodic analog SiO₂.

Synthesis of polymeric carbon dioxide has long been of interest to many chemists and materials scientists. The attempts, however, had not been successful for many decades, until very recently we discovered the polymeric phase of CO₂ at high pressures and temperatures. In this paper, we describe this polymerization along with the stability, structure, and mechanical and optical properties of CO₂. Our optical and x-ray results indicate that CO₂ has a highly non-linear generating the second harmonic of Nd : YLF laser at 527 nm and is also superfine similar to solid-O₃ polymers, and is quenchable at ambient temperature at pressures above 1 GPa.

* This work has been done in collaboration with W. G. Gygi, G. Galvani, V. Itoh, X. Bi, C. B. Hauker at LLNL, M. F. Nicol at UNLV, S. Carlson, D. Harnagin at EHSF and has been performed under the auspices of the US Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.


Ab initio time-dependent Hartree-Fock (TDHF) theory provides a simple and straightforward models to model optical materials. However, until recently, the application has been limited to molecular systems containing less than half a dozen atoms. Two recent advancements in the TDHF theory have, however, made it a technique of choice for modeling nanoscale optical materials from first-principles. The first has been the introduction of the (2n+1) rule of the perturbation theory in coupled Hartree-Fock (CHF) solution of TDHF equations. This allows calculation of (2n+1) th-order energy from the n-th order wavefunction, resulting in considerable savings of computational resources. The second major advancement has been the introduction of the direct approach of solving TDHF equations. In the direct-TDHF approach, the ubiquitous two-electron integrals (TEI) needed to construct Hartree-Fock matrices are calculated when and needed, thus obviating the need to store and process billions of TEI, as is done in the conventional compute-store-and-retrieve (CSR) approach. These developments also lend themselves to be easily adapted with other first-principles approaches, such as the unrestricted Hartree-Fock (UHF) for open-shell calculations and density functional theory. In this paper, we shall review the recent advancements in the TDHF theory and demonstrate its applicability by presenting results for the linear and nonlinear optical properties of nanoclusters consisting of group III (Ga) and group V (N, P, As) atoms. From the analysis of the results and a comparison with related experimental data, the merits and the demerits of the TDHF theory in modeling optical materials will be discussed. 1. S. P. Karna and M. Dupuis, J. Chem. Phys., 12, 487 (1991).

11:45 AM 6H.9 THE FIRST PRINCIPLES STUDY ON LIGHT EMITTING PROPERTIES OF SEMICONDUCTOR METAL SILICIDES. Kenji Yamasaki, Kazuki Masahashi, and Koichi Sawa, Central Research Institute, Mitsubishi Materials Corporation, Osaka, JAPAN.

Semiconducting metal silicides are potential candidates of silica-based light emitting materials [1]. In order to carry out meaningful screening of the candidates, we calculated the oscillator strength between the valence and excited states near the band gap for such silicides such as FeSi₂, CrSi₂, ReSi₂, Ru₂Si₃, OsSi₃, and MnSi₂. The electronic states were obtained by using a twodimensional band-perturbed-plane-wave method (FLAPW) [2] based on the local density approximation (LDA). The results show Ru₂Si₃ and Cu₂Si are direct gap semiconductors, while FeSi₂, CrSi₂, OsSi₃, and MnSi₂ are indirect gap semiconductors. Although, in experiments, FeSi₂, Cu₂Si, MnSi₂, and Ru₂Si₃ are reported as small gap semiconductors, the underestimation of the band gaps by LDA caused the closure of the gaps. Ru₂Si₃ and Cu₂Si have direct gaps at Γ point, but the values of the oscillator strength across the gaps are evaluated to be zero. Among the indirect gap semiconducting silicides, FeSi₂, OsSi₃, and MnSi₂ have several peaks and valleys facing each other near the band gap. Among the combinations of the facing peaks and valleys, we obtained the largest value of an oscillator strength of 0.3 at X point for OsSi₃ with band gap energy of 0.42 eV [1]. D. L. Leong, M. Harry, K. J. Reeson, and K. P. Horwood, Nature, 387, 686 (1997). [2] P. Blaha, K. Schwarz, and K. Luiz, WIEN97, Vienna University of Technology, Vienna 1997.

SESSION B7
Chair: James R. Melikian
Thursday Afternoon, December 29, 1999
Room 209 (H)

1:30 PM 6I.1 FIRST-PRINCIPLES CALCULATIONS OF NONLINEAR OPTICAL RESPONSE FUNCTIONS IN SEMICONDUCTORS.
Sergey N. Radev and Walter H.L. Lambrecht, Case Western Reserve University, Cleveland, OH.

We discuss recent progress in calculation of nonlinear optical response functions in semiconductors. Since the work of Sipe and coworkers [Phys. Rev. B 48, 11,705 (1993); ibid 52, 14366 (1995)] it became clear that the calculation of nonlinear optical response functions in crystals of general symmetry requires a careful distinction of pure inter-band and mixed intra-band contributions in the time evolution of the electron density operator under the influence of the electromagnetic field perturbation. We present our implementation of this approach using the linearized muffin-tin-orbital method and discuss its application to the calculation of second harmonic generation (SHG), the linear electro-optic (LEO) effect, and circularly polarized current injection. The importance of gap corrections beyond LDA is discussed. The relation of the second order response functions to the linear response function is illustrated and it is shown how band structure information is contained in these spectra with an example from SiC polytypes. As primary application, we discuss the SHG
coefficients of chalcogenides of both the II-VI and III-VI families. We show that the decomposition in inter- and intra-interband contributions leads to new insights in the reasons for the high $\chi^{(2)}$ of some of these materials. We also present results for LiGaO$_2$, a material with high band gap and discuss its applicability to frequency conversion into the UV. Supported by NSF.

2:00 P.M. B7.2
FIRST-PRINCIPLES CALCULATIONS OF POSITRON
ANNIHILATION IN SOLIDS: D. Barbieri, Northeastern Univ.,
Dept. of Physics, Boston, MA; M. Hinthih, JUT, Lab. of Physics,
Espoo, FINLAND; R. M. Nieminen, HUT, Lab. of Physics, Espoo,
FINLAND; M. J. Puska, HUT, Lab. of Physics, Espoo, FINLAND.

We present first-principles approaches based on the density functional theory for calculating positron states and annihilation characteristics in condensed matter. The treatment of the electron-positron correlation effects (the enhancement of the electron density at the positron with respect to the mean-field density) is shown to play a crucial role when calculating the annihilation rates. A generalized gradient approximation (GGA) takes into account the inhomogeneities of the electron density in the ion core region into account and reproduces well the experimental total annihilation rate (inverse of the positron lifetimes) by suppressing the rates given by a local density approximation (LDA). The GGA combined with an electron-state-dependent enhancement scheme gives a good description for the momentum distributions of the annihilating positron-electron pairs reproducing accurately the trends observed for deep core and uppermost d electrons in the II-VI compounds in the angular correlation (ACAR) or Doppler broadening measurements of the annihilation radiation. The reliability of the present positron lifetime and momentum density calculations yields a unique tool for defect identification in semiconductors. We will show that the identification of vacancy-impurity complexes in highly n-type Si is a particularly successful application.

2:15 P.M. B7.3
Abstract Withdrawn.

3:00 P.M. B7.4
SECOND-HARMONIC GENERATION IN SEMICONDUCTORS
AND INSULATORS. Zachary H. Levine, NIST, Gaithersburg, MD.

Over the past several years, the calculation the nonlinear susceptibility on a nearly first-principles basis has been created more or less from scratch. The key theoretical developments were a method to correct local-density functional band gaps, and the simple recognition that fairly accurate wave functions were required for reliable work. Calculations have been carried out for a number of crystals, including cubic semiconductors, SiC polytypes, Se, quartz, and others. One advance over an older generation of theories — the bond charge model — occurs in understanding III-V semiconductors.

3:30 P.M. B7.5
Abstract Withdrawn.

3:45 P.M. B7.6
THE INFLUENCE OF VACANCIES ON OPTICAL PROPERTIES
OF SiC NANOCRYSTALS. K. P. Plucinski, Military Univ. of
Technology, Electronics Dept., Warsaw, POLAND; I. V. Kityk,
Institute of Physics, WSP, Czestochowa, POLAND; A. Kasuba,
University of Maine, Le Mans, FRANCE; C. Charpentier, Univ.
of Maine, Le Mans, FRANCE.

The origin of vacancies in SiC nanostructures is not yet fully understood. It is important to devise a procedure for modeling such vacancies since they can significantly change the optical and electronic properties of SiC crystals. This feature could broaden possibilities for new development in opto-electronic devices. Most of the procedures that are currently used are based on an oversimplified crystalline-like approach. In the best case, the dependence of the total energy on particle size has been investigated. Most of the previous calculation approaches have been based on an simplified linear molecular orbital or on pseudopotential calculation of existing vacancy models without consideration for the surrounding atomic arrangement. A major objective of our work was to devise a model for vacancies which would make it possible to assess their influence on optical properties of SiC nanocrystals. Using a complex approach that included ab initio molecular dynamics simulation and calculations within the basis set of the norm-conserving nonlocal pseudopotential, we made calculations of the probability of a vacancy spin-polarized state occurring as a function of nanoparticle and grain sizes. The optimized structural geometry of the real interface was built upon the basis of a molecular dynamics procedure with dynamics boundary conditions. Using the optimized structure obtained we thus carried out optimization in the vicinity of the charged vacancies. We have shown a significant influence of the local geometry rearrangement on the symmetry of the surrounding atoms. We carried out numerical estimations of the corresponding isotropic spin-polarised wavefunctions and compared the results with experimental EPR data.