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PROPERTIES OF IONS IN GLASS

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OPTICAL PROPERTIES OF IONS IN GLASS

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Introduction

There is continued interest in the optical properties of ions in insulating glasses for various absorption, luminescence and quantum electronic applications.¹ Examples include selective absorption filters, scintillators and phosphors, photochromic glasses, lasers, and Faraday rotators. Materials with the desired optical properties for such applications have usually been found empirically - guided by knowledge of properties of related materials - or serendipitously. With time, simple cook and look approaches have evolved into giving the situation the penetrating look and coming up with the inspired guess. The question arises whether we are approaching the time now, or in the next twenty years, when reliable computational procedures can be developed to predict glass compositions having specific optical properties without this traditional reliance on empiricism.

The dependence of many physical properties on glass composition can be parameterized and predicted using additivity relations and parameters derived experimentally. This approach

has been known and used for many years.² The quality of the predictions and the range of their applicability depend upon the experimental data base and the type of terms and number of parameters in the expression for the property of interest.

Computational procedures which require extensive experimental data as input are not the type we want to consider here. Instead we address the much more difficult task of predicting optical properties of ions in glass from first principles given only the physics of the constituent atoms. Such an ab initio method is potentially the most powerful and flexible predictive technique. A key element in this approach is the availability of computers sufficient for large-scale quantum mechanical calculations and simulations.

Depending upon the application, the active ion may be a transition metal, rare earth, or post transition group element, thus vastly differing bonding and electronic structures must be treated. Spectroscopic properties of the dopant ion of interest include the electronic energy levels, absorption and emission spectra, cross sections, and radiative and nonradiative transition probabilities. The effects of vibrations and temperature on these properties are also of interest. Since most dopant ions enter the glass network as modifier cations, if we can treat them successfully, then calculations of electronic structure should be extensible to network forming and modifying cations and anions.

Hence the dependence of the fundamental absorption edge and refractive index of the host glass on composition and temperature should also be predictable.

An indication of the prospects for developing ab initio computational procedures can be gleaned from an examination of the encouraging, albeit gradual, progress made in understanding the properties of dopant ions in crystals. This is justified because, as Zachariasen noted many years ago,³ glass is merely a crystal with an infinitely large unit cell and containing an infinite number of atoms.

Optical Spectra in Crystals

After several decades of effort, accurate ab initio characterizations of the electronic structure of impurities in crystals are still elusive. Impurity levels are frequently well separated from those of the host crystal and thus can be treated as localized. Calculations generally fall into two categories: (1) prediction of wavefunctions for an ion in a given local geometry and (2) determination of the optimum geometry for a given impurity. Reference 4 contains a good survey of the state of the art in both of these areas.

Crystal field and ligand field theories have achieved some notable successes in calculating electronic energy levels, but these approaches involve parameterizing the field using a minimum number of terms consistent with the local symmetry. For most ion-host systems, attempts to predict crystal field parameters from first principles using electrostatic models is a well documented failure. Models intermediate between an entirely

phenomenological treatment and a complete linear-combination-of-atomic-orbitals calculation have been developed; examples of their successes and failures are discussed in Ref.5.

Molecular orbital calculations provide a more rigorous prediction of energy levels of ions in solids. Electronic structures can be examined using a variety of molecular orbital procedures including purely ab initio methods. Since the electron states associated with the impurity are localized on a few atoms, a small number of atoms may be used to model this region of the crystal in real space. These so-called cluster methods (reviewed in Chapter 6 of Ref.4) are very versatile. However, a problem associated with all cluster-type models is the treatment of atoms on the surface of the cluster and simulation of the crystal beyond the cluster. Several approximations have been used but definitive experimental confirmation of their appropriateness is missing.

Cluster molecular orbitals are generally expressed as linear combinations of atomic-orbital-like basis functions centered on the nuclei. As the number of required basis functions increases, the number of integrals to be evaluated and the amount of computer time needed escalates rapidly. As a consequence, pseudopotential techniques have been used. These techniques can be ab initio in form; no parametric functional forms are assumed and no experimental data is needed to construct them.*

Calculations of electronic properties requires that the atom positions about the impurity ion be specified. Structural simulations of crystals have ranged from simple oxides and alkali halides to complex minerals.⁴ Theoretical calculations involving minimization of the total energy have made possible the determinations of crystal structure, lattice constants, bulk moduli, and phonon dispersive curves. The methods can be ab initio and depend on pseudopotentials generated knowing only the atomic number of the constituent elements.⁴ When a dopant is introduced, it constitutes a point defect. Therefore treatment of lattice relaxation effects must be included to obtain proper positions of the surrounding atoms or those within a cluster. Structural simulations must also account for instabilities against symmetry or charge-state changes and the effect of electronic excitation since the structure of the neighboring ions may differ when the ion is in an excited state.

The reliability of calculations of static features, which depend on short-range order, and dynamic features, which depend on intermediate-range order, involve a delicate balance of energies and are limited by the quality of the interaction potentials used in the simulations.

Metal impurities in crystals can be treated using quantum mechanical methods developed for treating large molecules. Large basic set open shell Hartree-Fock calculations are currently being carried out for clusters of over 30 atoms.⁷ Computer codes are being expanded to include electron correlation, spin-orbit coupling, and configuration interactions. These powerful, modern theoretical methods are very promising but have yet to address all of the many issues mentioned above.

Optical Spectra in Glass

All atoms in a glass are structurally inequivalent. Therefore in the present context, glasses differ from crystals principally in that rather than having one or a few sites of specific geometry, there is a distribution of different local environments for the optically active ions. The resulting site-to-site variations in electrostatic, spin-orbit, and crystal field interactions produce a range of energy level separations and transition probabilities. These are revealed spectroscopically by inhomogeneously broadened linewidths and nonexponential excited-state decays. In glass lasers, differences in the microscopic structure at the lasing ion sites lead to spectral and polarization hole burning effects.⁸

Most spectroscopies used to investigate ions in glasses such as nuclear and electron spin resonance, Raman, and optical techniques yield information about the entire ensemble of physically different sites;⁹ details about individual sites are not provided. Laser spectroscopy, in contrast, can be used to selectively excite and study specific subsets of ions - those in sites having energy levels in resonance with the laser wavelength. (These subsets may still contain large numbers of sites.) Techniques such as laser-induced optical site selection spectroscopy and fluorescence line narrowing¹⁰ and photophysical and photochemical hole burning¹¹ provide unique capabilities to probe impurity sites with extremely fine spectral and temporal resolution. The degree of site selectivity depends on the ratio

of the natural or homogeneous optical linewidth to the inhomogeneous linewidth. Experiments using rare-earth ions and transitions having homogeneous linewidths very much smaller than the inhomogeneous linewidth in glass clearly demonstrate the existence of large numbers of physically different sites.¹⁰

Although site-selective laser spectroscopy provides unique information about ions in glass, both the local structure and resultant fields must be known to predict the optical spectra. The comments made earlier about the prospects for ab initio calculations of electronic properties of ions in crystals are again apropos for glasses. Calculations for glass, however, are hampered further by our lack of knowledge of the local geometry, its variation from site to site, and its dependence on chemical composition.

Simulation of Glass Structure

Molecular dynamics, which has been used extensively in studies of liquids, has also been used to simulate local atomic arrangements about modifier cation sites in simple and multicomponent glasses.¹² The simulation begins by specifying the initial positions of a group of ions, their velocity distribution characteristic of a specific temperature, and the interatomic potentials. Newton's equations of motion are then solved numerically to find new positions and velocities at a later time. The time steps are typically in the order of femtoseconds (less than a vibrational

period). About $10^3 - 10^4$ steps are used to generate an equilibrium fluid. To simulate a glass, one or more structural configurations of the fluid are quenched in a series of step reductions of the temperature. The low temperature configuration may be further relaxed to a local energy minimum.¹³ The collection of structures resulting from many such simulations is assumed to represent the range of local environments present in the glass. Both radial and angular information about pairs or larger groups of ions can be calculated from the simulated structures.

Computer simulations of glass have several limitations. First, because of cost the total time of the simulation is typically very short, less than 1 nanosecond. The cooling rates are therefore very much faster than those of laboratory prepared glasses and the simulated structures are expected to be more disordered.¹⁴ Second, the interaction potentials used thus far have been spherically symmetric consisting of Coulomb and exponential repulsion terms. The strength of these interactions are not known apriori and are adjusted based upon experimental data or estimated crystal properties. Finally, the size of the systems that can reasonably be treated with present-day computers is about 10^3 particles. To reduce surface effects, periodic boundary conditions are imposed. While this may be adequate for treating localized impurities, larger systems are needed to treat extended defects or those occurring with low probability.

Computer simulations using molecular dynamics methods have other applications. Since they also provide kinetic information, they can be used to investigate properties such as vibrational modes and their effects on optical spectra. Vibrational spectra have been calculated either by direct diagonalization of the dynamical matrix for the glass or from autocorrelation functions computed directly from the simulations.¹³ Quench echoes, which occur in computer models of glassy solids, offer a further technique for studying dynamic behavior.¹⁸ Striking differences in the low-temperature properties of crystalline and amorphous solids have been attributed to low energy excitations, known as two-level systems.¹⁶ The microscopic nature of these excitations and how they are related to various physical properties of glass are unknown, but could be investigated using large-scale computer simulation techniques.

Validation of the simulated structures of glass is limited because no measurement is capable of specifying the three-dimensional structure uniquely. Satisfactory agreement has been found between predicted average coordination numbers, neighbor distances, and bond angles and results of x-ray and neutron diffraction studies.¹² The structure about a specific ion and partial distribution functions, which are of interest here, can be explored via NMR, EXAFS, neutron scattering with isotopically enriched samples, and x-ray scattering using synchrotron radiation and anomalous dispersion effects.¹⁷ Preliminary investigations show general agreement with the simulated local structures but

more detailed comparisons with experiment are needed. Predicted bond angle distributions do not appear to be reliable using only radially dependent forces.¹⁸

Optical spectra have also been compared with computer simulations using simple electrostatic models of the crystal field.¹⁷⁻²⁰ Although qualitative agreements are obtained, accurate calculations and simulations of both the local structure and electronic energy levels are required to interpret optical spectra in glass, features that have been treated with only limited success to date in crystals.

Conclusions

Is there hope that we will ever be capable of simulating atomic structures comparable to those actually occurring in laboratory and production glasses and of calculating the electronic properties of both an impurity ion and the host glass from first principles? A unified treatment of structure and optical properties of the host and dopant ion is in the offing. It is therefore not a question of possibility but rather one of probability within a given time span. Large increases in computing power - greater speed and larger storage capacity - and faster algorithms will undoubtedly appear and should make possible the simulation of systems of sufficient size to include most excitations and defect structures of interest.

The answer to the above question will continue to be guided by progress made in treating crystalline materials and by the success of various potential models in predicting equilibrium positions of ions, charge states, dynamic properties, and electronic structures of the host and impurity ions. I believe it is probable that in twenty years we will have reliable procedures for predicting optical properties of ions in crystals.

The development of corresponding procedures for predicting the properties of complex, multicomponent glasses within two decades is a herculean task. I am less sanguine about the probability of achieving this goal before Professor Kreidl's 100th birthday. But even if the ab initio methods are not totally reliable in making quantitative predictions, they should still be useful. Less heroic predictions of the general trends of properties with composition should be possible and should offer valuable guidance in compositional studies.

An important question to be asked is the cost effectiveness of computer simulations in comparison to laboratory experiments.

K. G. Wilson noted recently that "Computer simulation, when feasible, is usually the least expensive and most rapid method available for prototyping and optimization of new products and processes".

He added "It takes many years of practical experience with large scale computing to be able to make sensible decisions or provide sound advice on simulation matters".²¹ The remainder of this millenium would seem to be the minimum expectation of the time necessary to reach this stage in the simulation of optical properties of ions in glass.

More detailed and critical experimental tests of computer simulations involving both evolutionary and revolutionary developments are certain to occur in the future. Angle-resolved photoelectron spectroscopy in the VUV and x-ray regions using synchrotron radiation and inverse photoemission techniques are greatly enhancing experimental studies of electronic structures of complicated solids. Atomic-resolution electron microscopy and nanometer-scale electron microdiffraction should yield important structural information about amorphous materials. Laser spectroscopy with spectral resolution measured in Hertz and temporal resolution measured in femtoseconds is possible today. Combined with multiple excitation schemes, unique site specific information should be obtainable. Optical dephasing studies using photon echoes have recently been used to investigate two-level systems and tunneling modes in glass.²¹ The above techniques and other as yet unexpected techniques will be the final arbiters in establishing the validity of large-scale computer simulations for screening and predicting new glass compositions.

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