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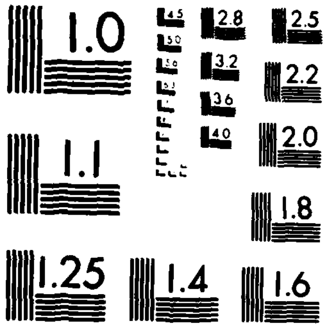

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In an attempt to understand mobility mechanisms, to predict optimal conduction conditions for solid electrolytes, and to develop methods for calculating conductivity in classical many-body systems, calculations have been completed for a variety of one-, two-, and three-dimensional model lattice systems. These calculations involve Monte-Carlo simulation, self-consistent-field techniques, and reduced Langevin dynamics, and have been devoted to the actual calculation of the frequency-dependent conductivity tensor $\sigma(\omega)$, and of

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20. ABSTRACT CONTINUED

its variation with important experimental variables (concentration, pressure, temperature, trap sites, identity of mobile ion, lattice geometry). We have characterized the relationships among conduction mechanism, carrier density, ion potentials, and observed response. We have examined the extent, importance, and effects of ion-ion coulomb correlations, which increase conduction in incommensurate cases. We have examined the role of compensators and the extent to which trapping inhibits conduction. The interrelationship of static lattice potential, ion-ion repulsion, stoichiometry, and conduction has been articulated. Finally, we have continuously modified our computational efforts on the basis both of the emerging mechanistic picture and of constant interaction with and testing by local experimental groups.

The ambition of this research has been to provide hard numerical data for three purposes: understanding and prediction of the effects of variation of external parameters (temperature, doping, compensation, ion exchange) on conductivity, comparison of good numerical data with extant formal theory to focus on the most important variables or achieving optimal conductivity, and development of a mechanistic model (including such extremes as hopping and liquid-like diffusion) to correlate the behaviors of a large number of framework conductors. We believe that these ambitions have been satisfied quite well: we have explained extant experiments and predicted new conductivity features for such important ionic conductors as β''-alumina, NaI-poly(ethylene oxide), crystalline and glassy β-eucryptite, and NASICON. In addition, we have developed new theoretical approaches, notably the trajectory-bundled time-dependent self-consistent-field method, and dynamic percolation theory, which promise to be very efficient for planned future research on ionic conductivity at interfaces, in glasses, and in alloy solid electrolytes.

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Solid Electrolytes: Mechanisms for Achieving Optimal Conductivity

Final Report

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Contents

Statement of Problem:

Solid electrolytes, or fast-ion conductors, are under intense scrutiny in a number of industrial, government, and academic laboratories for applications in fuel cells, in stable, long shelf-life primary batteries, and, especially, in high energy-density, stable secondary batteries for vehicular propulsion. Our research efforts have been directed at the understanding of the mechanisms by which conductivity occurs in framework solid electrolytes, and at possible means of enhancement of the conductivity by selection of different experimental or performance conditions, involving control of such variables as ion density, bulk density, temperature, crystallinity, and counterion. The problem, then, might best be defined as: Mechanistic Understanding of Ionic Conductivity, and Enhancement Mechanisms for Ionic Conductivity, in Framework Solid Electrolytes.

Abstract of Progress

In an attempt to understand mobility mechanisms, to predict optimal conduction conditions for solid electrolytes, and to develop methods for calculating conductivity in classical many-body systems, calculations have been completed for a variety of one-, two-, and three-dimensional model lattice systems. These calculations involve Monte-Carlo simulation, self-consistent-field techniques, and reduced Langevin dynamics, and have been devoted to the actual calculation of the frequency-dependent conductivity tensor $\sigma(\omega)$, and of its variation with important experimental variables (concentration, pressure, temperature, trap sites, identity of mobile ion, lattice geometry). We have characterized the relationships among conduction mechanism, carrier density, ion potentials, and observed response. We have examined the extent, importance, and effects of ion-ion coulomb correlations, which increase conduction in incommensurate cases. We have examined the role of compensators and the extent to which trapping inhibits conduction. The interrelationship of static lattice potential, ion-ion repulsion, stoichiometry, and conduction has been articulated. Finally, we have continuously modified our computational efforts on the basis both of the emerging mechanistic picture and of constant interaction with and testing by local experimental groups.

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liquid-like diffusion) to correlate the behaviors of a large number of framework conductors. We believe that these ambitions have been satisfied quite well: we have explained extant experiments and predicted new conductivity features for such important ionic conductors as β''-alumina, NaI-poly(ethylene oxide), crystalline and glassy β-eucryptite, and NASICON. In addition, we have developed new theoretical approaches, notably the trajectory-bundled time-dependent self-consistent-field method, and dynamic percolation theory, which promise to be very efficient for planned future research on ionic conductivity at interfaces, in glasses, and in alloy solid electrolytes.

Summary of Results

We have obtained significant results in two closely related areas:

(a) Mechanisms of Ionic Conductivity, in crystalline frameworks, including possible conductivity enhancement (papers 1,2,3,8,9,13).

(b) Development of Techniques for Calculation of Ionic Conductivity in non-crystalline environments (papers 4,5,6,7,10,11,12).

These efforts have involved different techniques, personnel, and ambitions. The mechanistic work (a) largely involved use of techniques which we and others had previously developed (notably Langevin dynamics and Monte-Carlo simulation) to study conductivity mechanisms and enhancement both in such actual systems as NASICON, Na^+ β'' alumina, Ba^{++} β'' alumina and β-eucryptite. The technique-oriented work (b) was aimed at extending the capability for mechanistic investigation to highly disordered materials, in particular to the glassy framework electrolytes whose development (largely in British and French laboratories) has been one of the most exciting new developments in the solid electrolyte area. In these materials, the framework lattice is not periodic, so that the treatments of the framework either as the provider of a periodic lattice for hopping (on which the Monte-Carlo work is based) or as the source only of periodic (static) and random (dynamic) potentials (on which the Langevin dynamics work are based) become invalid. Both the dynamic percolation (papers 7,11) and self-consistent-field (papers 4,5,6,10,12) methods can treat this disordered problem, and we have, in fact, applied the former to polymeric electrolytes.

This summary will discuss these two areas of research independently, although they actually comprise two parts of an integrated effort on mechanisms of ionic conductivity in ordered (a) and in disordered (b) lattices.

For convenience, we have collected the abstracts of our publications as Appendix A, to which the reader may refer in connection with this summary.

(a). Mechanisms of Ionic Conductivity, and of Conductivity Enhancement, in Crystalline Framework Solid Electrolytes.

The crystalline framework electrolytes are, technologically, the most important class right now; β aluminas are the electrolyte for the advanced sodium/sulfur battery. All of the crystalline frameworks are characterized by well-defined conduction-path structures, usually within a reduced dimensionality (sheets for β-alumina, tunnels for NAISCON and for β-eucryptite). There exists a good separation in time scale between lattice vibrations ($\sim 10^{-14}$ sec) and ionic hopping times ($\sim 10^{-12}$ sec), so that Langevin dynamics, with no memory effects, is a valid model for the ionic motion. The equations of motion are then

$$m\ddot{x}_i = -\nabla_i \{V(x_i)\} + R(t) - m\Gamma\dot{x}_i \quad . \qquad (1)$$

Here the ionic carrier at position x_i has mass m, and is subjected to three forces: that derived from the potential (including both coulombic and framework terms) and the random (R) and damping (Γ) forces arising from the lattice motion. By using the full coulomb many-body potential in V, we have studied mechanism and dynamics of ionic motion in tunnel conductors (papers 1,2,3,9).

The ionic carriers in framework solids are usualliy fairly light (Na^+,Li^+) so that their motion is not overdamped. Paper 1 uses both Langevin simulation and experimental data (absorption spectra) to show that the dynamics of these carriers cannot be calculated by simply assuming rapid momentum equilibration, or replacing Langevin by Smoluchowski dynamics. It also defines a possible effective-potential model for use in defining a simple, one-body picture of the carrier dynamics in such systems.

Paper 2 includes an overview of the conduction mechanisms in a number of solid electrolytes. In particular, it stresses the substantial differences expected between motion in a commensurate stoichiometry (where the number of lattice sites is an integral multiple of the number of carriers) and in an incommensurate case (where the multiple is not integral). This notion is deepened considerably by the calculations of paper 3, in which it is shown that the local minima in the $\sigma-\rho$ (conductivity/density) plot observed for commensurate cases always correspond to hopping behavior, and that coulomb correlations will, for this situation, always reduce the conduction. Conversely, incommensurate systems can, for strong enough correlations, move the ions by a collective, liquid-like mechanism, and here coulombic repulsion can actually lead to <u>increased</u> conductivity. This suggested that carriers with high charges moving in a framework with highly incommensurate stoichiometry should conduct well; concomitant experimental work by Whitmore and his students is investigating this situation.

Paper 9 applies the Langevin technique to study carrier trapping by counterions or by crystal defects. We show that the nonperiodic, deep-well potentials due to these entities compete with the periodic framework potential and with the interionic coulomb repulsion to produce very unexpected behavior. By trapping one or more carriers, these deep-well potentials can render a formerly commensurate density effectively incommensurate, thus actually <u>increasing</u> the overall conductivity by trapping some carriers! For incommensurate, good conductor situations, on the other hand, the trapping does indeed reduce the conductivity.

The Langevin dynamics method has several advantages; in particular, it gives the conductivity for all frequencies, rather than just at DC. Our studies have thus been useful for comparison with optical and microwave spectra, as well as with overall dc conduction, and, as such, have helped clarify such concepts as attempt frequencies, correlation factors, and collective effects.

For the particular case of β'' aluminas, there has been a great deal of experimental study of conductivity under a variety of conditions. For this particular system, moreover, the hopping model is well justified by the height of the barrier and the vacancy mechanism of dc transport. Accordingly, we have used a generalized form of the Monte-Carlo method to analyze conductivity in several β'' alumina systems. Paper 8 considers the quasiparticle description of conduction near the half-filled lattice case ($\rho \sim 0.50$) appropriate for Pb^{++} or Ba^{++} or Ca^{++} β'' aluminas. We find two "superdefects" which dominate the conduction. Both form on the superlattice which consists of the alternate sites (every second site) of the physical β'' alumina Beevers-Ross lattice. At low temperatures, the "superinterstitials" dominate conduction for $\rho > 0.50$, "supervacancies" for $\rho < 0.50$. While the latter exhibit low mobility, the former are very mobile, and, accordingly, the optimal stoichiometry for highest conductivity increases from $\rho = 0.50$ at very high temperatures to $\rho = 0.67$ at low temperatures, as correlation effects become important and superinterstitial hops, rather than independent ion hops, provide the effective step for conductivity. In further work to be published, we extend this notion to the analysis of low-angle scattering data, ordering phase transitions, and relaxation-time behavior in these β'' aluminas.

Several experimental groups have prepared β'' alumina structures with two different mobile species present in the conduction plane. In paper 13, we employ the Monte-Carlo technique to analyze the expected conductivity phase diagram for the Ba^{++}/Na^{+} β'' alumina case. We find that, as the Ba^{++} ion exchange process begins, Na^{+} conduction first increases as the number of available vacancies grows, then decreases due to strong correlation effects. Once again, a point of optimum conductivity is found, and once again it is temperature-dependent. For reasonable temperature ($T \cong 300°C$), the conductivity maximizes for an ion exchange of about 30% of the initial Na^{+} ions present; again, experimental work is under way in Whitmore's group to investigate this prediction.

These mechanistic studies have accomplished three aims: they have demonstrated that Langevin dynamics and hopping models are useful techniques for studying ionic conductivity (and that Smoluchowski dynamics is less useful), they have furnished mechanistic understanding of the published experimental work on framework electrolytes, and they have predicted conditions under which maximal conductivity can be achieved for these materials.

(b) Development of Techniques for Calculations of Ionic Conductivity in Non-Crystalline Environments

The crystalline framework conductors described above have dominated experimental work on fast-ion conductors until quite recently. Since 1981, however, there has been growing interest and activity in the area of polymeric and glassy solid electrolytes. In these materials, both the mobile-ion array and the underlying framework lattice are highly disordered. For such materials, the Langevin and hopping models become difficult to apply. Accordingly, we have been developing new theoretical methods to deal with these systems.

The essential nature of ionic motion in such glassy framework conductors as glassy β-eucryptite or NASIGLAS or $Li_2O/Br_2O_3/SiO_2$ involves coulombically-correlated mobile ions moving in a highly structured but disordered background. The theoretical approach for study of such a system would involve first accounting for the coulombic correlations to define an effective one-particle static or dynamic potential for the ionic motion, and then to embed the resulting single effective-particle dynamics in the disordered potential of the glassy framework. We have taken a significant step toward the development of such a one-particle effective potential by means of the static and time-dependent semiclassical self-consistent-field (SCF) method, which is presented and applied to some small-system test cases in papers 4,5,6, and 12.

The idea of these SCF studies is a simple one. If the wavefunction for a system of N particles is approximated as a simple product:

$$\Psi(x_1,x_2\cdots x_n) \equiv \prod_i \phi_i(x_i) \qquad (2)$$

with ϕ the single-particle functions and x_i the coordinates of particle i, then the variational principle yields Hartree-like equations of motion for the individual particles

$$[h_i(x_i) - \varepsilon_i(x_i)]\phi_i(x_i) = 0 , \qquad (3)$$

where ε_i is the energy of the i^{th} particle, and the effective hamiltonian is given by

$$h_i = T_i + \Big\langle \prod_{j\neq i}{}' \phi_j(x_j) \Big| V_{TOT} \Big| \prod_{j\neq i}{}' \phi_j(x_j) \Big\rangle , \qquad (4)$$

with T_i the kinetic energy of the i^{th} particle. Thus each particle moves in a field defined by the average of the other particles. If ϕ_i is taken as time dependent, then (3) becomes a dynamical result:

$$\frac{i\hbar\, \partial\phi_i(x_i,t)}{\partial t} = h_i(x_i,t)\,\phi_i(x_i,t) \quad . \qquad (5)$$

In papers 4, 6 and 12 we apply the static SCF result (4) to the analysis of vibrational states for three coupled particles. We develop the semiclassical techniques needed to solve (4) for realistic systems, and consider the choice of coordinate systems in which the problem is best solved. Paper 6 is of particular interest for applications to framework glasses, since it analyzes the occurrence of structural instabilities and ordering due to vibrational motion; similar ordering phenomena are observed in frameworks, and it will be of real interest to see if they survive in the disordered background potential of a glass. This paper also deals with the possible definition of collective coordinates for problems involving a large number of modes; analysis in terms of such coordinates might prove particularly useful in extended systems such as those in glassy electrolytes.

In some disordered electrolytes, conductivity beomes efficient only above the glass transition temperature; these systems include polymeric electrolytes based on poly(ethylene oxide) salt complexes. For these materials, the entire idea of hopping on a quasistatic lattice is invalid, since the disorder of the host material in which the ions move is dynamic rather than static. Then the ordinary theoretical tools used to study ionic motion will all fail, since the entire lattice becomes dynamically, rather than statically, defined. The only approach to this problem which has been used in the literature is based on quasithermodynamic constructs, notably the free-volume and configurational-entropy models. We have developed a microscopic picture for ionic motion in these materials, based upon a dynamic percolation model for the ionic motion. The model is characterized by two timescales, one defining the time for the ion to jump from one coordination geometry to another, and the second corresponding to the time for configurational changes to occur in the polymeric framework; this latter is called the renewal time, and glasses and ceramics are typified by an infinite renewal time.

In paper 7, we compare the predictions of dynamic percolation theory with free-volume ideas; the free volume is in fact correlated with the renewal time, and zero free volume corresponds to curtailed configurational freedom, to infinite renewal time, and to zero conductivity. The dynamic percolation picture is richer and more reflective of the real systems, however, since there are, in fact, two microscopic motion parameters in these systems. In particular, the kinetic effects of free-volume motion are present in the percolation, but not in the free-volume, formulations. This becomes important when long-range motions such as dc conductivity are considered, since the moving ion must see the open channel in the direction in which it wants to move rather than in any arbitrary location in the lattice. This notion of correlated lattice motion, a natural one in the dynamic percolation scheme, is entirely absent in the (statistical) free-volume or configurational entropy pictures.

Finally, we have examined the frequency-dependence of the ionic conductivity in the dynamic percolation model (paper 11). This is of real interest, since the nmr, optical, and microwave investigations of these materials have been among the most complete experimental studies, and since the quasithermodynamic approaches are inherently unable to deal with any dynamic phenomena. We find several interesting formal properties of the dynamic percolation picture; one of the most intriguing is a convincing proof that the renewal frequency γ and the applied field frequency ω enter into the final conductivity expression only in the combination $(\omega + i\gamma)$. Thus renewal of the lattice affects the hopping ions like an applied field of complex frequency.

We can also show that even in reduced dimensionalities in which static percolation is a finite-length process (that is, no diffusion occurs below the percolation threshold), the dynamic percolation picture, in agreement with experiment, always exhibits diffusive behavior, with the mean-square displacement a linear function of time. This dynamic percolation model is, so far as we are aware, the only microscopic technique for studying ionic conductivity in dynamically-disordered materials, and we intend to pursue further its implications for mechanism, for optical conductivity, and for the importance of local trap sites.

These studies of methods for dealing with highly-disordered electrolytes should, we feel, be as useful and helpful for dealing with some of the very newest materials (such as polymeric and glassy electrolytes) as the Langevin and Monte-Carlo methods have proved in study of the crystalline framework materials. We thus feel that this project has provided both numerical and mechanistic insights and some methodological advances for the study of solid electrolytes.

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Vibrational Levels in the Self-Consistent-Field Approximation with Local and Normal Modes. Results for Water and Carbon Dioxide

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Calculations are presented for vibrational energy levels of nonbending H_2O (at correct and linear geometries) and for linear HDO, DTO, $C^{16}O_2$, and $C^{16}O^{18}O$. Results obtained from accurate numerical studies are compared to those generated by using the self-consistent-field (SCF) approximation in both normal and local coordinates. We find that for all cases except H_2O, SCF corrections systematically and considerably improve the zero-order uncoupled normal-mode eigenvalues and render them superior to the local modes even for part of the vibrational overtone region of HDO and DTO. For H_2O, the local-mode picture remains better than SCF, due partly to the small size of the Wilson coupling in local modes (or equivalently to the near-degeneracy of the normal modes). These results demonstrate the quality of the SCF as the best independent-mode approximation. Moreover, unlike the cruder decoupled-mode results, the SCF frequencies are in many cases of nearly spectroscopic accuracy.

I. Introduction

The use of a local-mode description of vibrational states was developed by Henry and Siebrand, first in the context of radiationless decay[1] and later for characterization of the overtone region of X···H (X = O, C, N) stretches in several molecules.[2] More recently, a number of workers have used local modes for both theoretical and experimental study of the X···H overtone region; we cite specifically the elegant work of Swofford, Long, and Albrecht;[3] extensive applications and analysis have been presented by Sage[4,5] and by Wallace.[5] Although the local-mode picture is principally used in the overtone region, Gelbart and coworkers have pointed out that, in certain instances, even the fundamental absorption line may be best characterized by local modes.[6] More formal studies of local modes and their relation to normal modes were carried out by Brumer and Jaffe,[7] who showed that, in a classical two-mode model, a rigorous distinction can be drawn between local- and normal-mode behavior based on the characteristics of Poincaré surfaces of section. Lawton and Child,[8] using classical trajectories, have studied the local- and normal-mode behavior of H_2O and observed the transition from normal to local as energy increases.

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Dissociation dynamics of vibrationally excited van der Waals clusters: $I_2XY \rightarrow I_2+X+Y$ (X, Y=He, Ne)

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The dynamics of sequential dissociation processes of the type $XI_2(v)Y \rightarrow X + I_2(v')Y \rightarrow X + Y + I_2(v'')$ (X,Y = Ne, He) are studied using classical trajectory calculations and a recently presented classical version of the time-dependent self-consistent field (TDSCF) method. The results obtained indicate the presence of significant dynamical correlation effects of the rare-gas atoms on each other despite the negligible direct interaction between them; this is in qualitative agreement with experimental findings. Good agreement is found for the rate constants and the variation with rare gas as well as the branching ratios ($NeI_2He \rightarrow NeI_2 + He$ vs $\rightarrow I_2He + Ne$) calculated from TDSCF and from classical trajectories. Both classical trajectories and TDSCF show an essentially impulsive dissociation mechanism, in which dissociation typically follows a considerable number of vibrations, and is due to a relatively rare internal hard collision between an I atom and the rare gas. As in the three-body I_2X case, this mechanism differs from that in the RRKM strong coupling model. Energy- and momentum-gap relations, based on the weak-coupling picture, are found to be relatively successful but fail to describe the dynamics quantitatively.

I. INTRODUCTION

Among the most detailed measurements of the rates of unimolecular decay of molecules are the classic experiments of Levy and co-workers[1-5] on the vibrational predissociation of van der Waals clusters involving rare gases and I_2. For HeI_2, for example, the experiment involves the following three steps:

$$HeI_2(X\,{}^1\Sigma) + h\nu \rightarrow HeI_2(v',\ B\,{}^3\Pi_{0u}^{+}) , \tag{1}$$

$$HeI_2(v',\ B) \rightarrow He + I_2(v'',\ B) , \tag{2}$$

$$I_2(v'',\ B) \rightarrow I_2(X) + h\nu'' . \tag{3}$$

By measuring the absorption linewidth associated with Eq. (1), the rate of decay of the initially prepared complex is determined.[2] Measurement of fluorescence in step (3) provides vibration-rotation distributions associated with decay of HeI_2.[1] Since the initial state of v' may be varied simply by changing the excitation frequency ν, it is possible to map out both the decay rate and I_2 vibrational distribution as a function of initial energy.

In addition to the triatomic complexes HeI_2, NeI_2, ArI_2, etc., a number of tetratomic and larger complexes have been studied[3-5], including He_2I_2, Ne_2I_2, $HeNeI_2$, $ArHeI_2$, and Ar_2I_2. In this case, the absorption linewidth measures the rate of the first atom dissociated, and the I_2 fluorescence determines the I_2 vibrational distribution after all rare gas atoms have dissociated. Measurements on tetraatomic clusters have made it possible to study such questions as the importance of correlation between different dissociative steps, and the nature of energy migration between different bonds.

The wealth of data provided by these experiments has prompted several theoretical studies of vibrational predissociation, all of which have thus far been directed at triatomic dissociation using reduced dimensionlity models (either collinear or T-shaped). These include the early work of Child,[6] the coupled channel and distorted wave studies of Beswick and Jortner,[7] the Golden-Rule model of Ewing,[8] the quasiclassical trajectory calculations of Woodruff and Thompson,[9(a)] the perturbed-wave-packet study of Viswanathan *et al.*,[9(b)] and the time-dependent self-consistent-field treatment of Gerber *et al.*[10] While some of these theories are not intended to be quantitative, it is significant to note that there is good agreement between the lifetimes predicted by the coupled channel and the trajectory methods for collinear HeI_2.[9] Agreement of the HeI_2 coupled channel rate constants with experiment is also pretty reasonable[7(a)] [illegible] the T-shaped model and a potential composed of sums of Morse functions. Of course it should be remembered that the parameters in the potential are not known independently, and thus are adjusted to fit experiment in making comparisons. Other theoretical studies of vibrational predissociation in van der Waals molecules include Cl_2-Cl_2 by Brady *et al.*[11] and Ar–HCl by Child[12] and Dunker and Gordon,[13] and $Ar \cdots N_2$, HeI_2 by Shapiro.[14] In addition, Rice and co-workers[15] have studied $He + I_2$ collisions at energies only slightly above the dissociation threshold. In none of this work has the competition and correlation between different decay channels in a polyatomic dissociation process been examined.

In this paper, we use a combination of quasiclassical trajectory methods and time-dependent self-consistent-field (TDSCF) methods[10] to study vibrational predissociation in collinear models of the tetra-atomic clusters He_2I_2, Ne_2I_2, and $HeNeI_2$ and the triatomic clusters HeI_2 and NeI_2. The isomers $He-I_2-Ne$ and $HeNe-I_2$ are both considered. There are two purposes for our calculations: First, we are concerned with mechanistic questions, such as the applicability of simple impulsive

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Dynamical instabilities and structural changes in molecules

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Structural instabilities in molecular clusters have been observed in several recent classical simulations. They arise from changes in the dynamical interactions among the vibrational modes as energy increases and are entirely unrelated to vibrationally-induced instabilities of Jahn–Teller type. We show that the self-consistent field (SCF) approximation for vibrations provides a simple predictive model for such instabilities, in which the onset of instability is shown to arise from changes in the effective (mean) potential acting on each mode, as the total energy changes. Exact classical dynamics was used to test the SCF prediction for a simple two-mode model, with the result that the instability onset is correctly predicted by the SCF approximation. We comment on the relevance of these mean potentials for characterizing related phase transitions in clusters.

1. INTRODUCTION

There is considerable current interest in the question of structural instabilities in molecular cluster systems, with special attention focused on the relationship of such instabilities to phase transitions in the macroscopic limit. Nearly all the evidence for such transitions comes from classical numerical simulations, using both Monte Carlo and molecular dynamics methods, on molecular clusters. For example, Etter *et al.* [1] have investigated $(CO_2)_n$ for $2 \leqslant n \leqslant 13$. They observed that even for $n=2$, the cluster shows an instability (or structural change) as a function of energy (or of temperature); the instability becomes more pronounced as the size n increases. A qualitatively similar pattern was observed in the work of Nauchitel and Pertsin [2] on noble-gas clusters. They commented on the possible relationship of such structural changes to solid–solid and solid–liquid phase transitions in the corresponding macroscopic materials. An interesting paper by Rao, Berne and Kalos [3] studied both thermodynamic and structural properties of finite clusters in a search for transition behaviour; their figures show striking changes of orientational arrangement as a function of energy. Earlier investigations [4] focused

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Polymeric Solid Electrolytes: Dynamic Bond Percolation and Free Volume Models for Diffusion

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Polymeric solid electrolytes offer a difficult problem from the viewpoint of understanding the charge transport mechanism. While quasithermodynamic theories (configurational entropy, free volume) are useful for rationalizing the behavior of these materials, they do not really amount to a microscopic picture. We have developed a dynamic bond percolation (DBP) model to describe ionic conductivity in these materials. The DBP model is based on a master equation describing ion hops among sites. The percolation aspects are included by making the bonds between sites randomly open or closed. The dynamical aspect is due to the configurational motions of the polymer, and results in the variation of the bond assignments as open or closed. The relationship of DBP to free volume theory is sketched; this involves a specific consideration of kinetic effects on free-volume motion.

I. Introduction

Since their discovery by Wright [1] and early exploration by Armand [2], polymeric solid electrolytes have been the focus of intense investigation in several laboratories. Many interesting observations have been reported, including vibrational spectra leading to a solvation scheme for the cations [3], thermochemical studies implying a salt lattice energy threshold for complex formation [2,4], network studies showing the increase of conductivity with decreasing glass transition temperature [5], electrochemical studies showing both negligible electronic conductivity [6] and significant anionic and cationic motion [7], microwave conductivity data indicating similarity of free polymer and polymer-salt complex response for frequencies above 0.5 GHz [8], morphological and thermal analysis studies indicating mesophase behavior [9], activation studies showing an important role for salt-free polymer in the conductivity [10], viscoelastic studies showing an increase in glass transition temperature with salt concentration [2,11], and a number of new polymer hosts [11,12] in addition to the original materials, polyethylene oxide (PEO) and polypropylene oxide. The interpretation of the conductivity in these largely amorphous polymeric materials, which are generally studied well above their glass transition temperatures T_g, is nearly always given, following Armand [13], in terms of the Vogel-Tammann-Fulcher (VTF) equation of glass science [14] or, more extensively, in terms of the free volume theory (FVT) of Cohen and Turnbull [15,16].

The VTF equation itself is of empirical origin, though it can be derived [15] straightforwardly in the context of FVT. The VTF equation for the conductivity σ of a polymer/salt complex may be written

$$\sigma = A_0 T^{-1/2} e^{-E_A/k(T-T_0)} \qquad (1)$$

Here A_0 is a (weakly) temperature dependent prefactor, and T_0 is the so-called equilibrium glass transition temperature [17,18]; E_A has the form of an activation energy. Equation (1) predicts precisely the type of curved activation plot ($\ln \sigma T$ vs T^{-1}) actually observed for many [13] of these complexes, though hysteresis [11] and complications due to uncomplexed polymer [10] may be observed in certain temperature and stoichiometric regimes. Because eq. (1) may be derived from FVT [15], and since it characterizes the conductivity of most PEO-salt complexes fairly satisfactorily, it is now quite standard to use FVT to discuss the ionic conductivity of polymeric solid electroltytes. There are, however, several drawbacks to the FVT approach. Most importantly, it is not intended to apply to the diffusion of small ions within a solid comprised of much larger polymeric chain segments (nor, originally, to polymers themselves, for which a configurational entropy model [19-22] is in several senses preferable); rather, it is used to describe viscosity, thermodyanmic data, and relaxation behavior of glass-forming materials [15,16,23-25]. While its extension to neat polymers may, with caution, be carried out, its extension to ionic motion within polymers is more problematic. In particular, one of the fundamental assumptions of FVT, the facile and rapid redistribution of the free volume, may fail to hold in the case of polymer electrolytes with low fluidity.

We have recently presented a microscopic theoretical treatment of ionic motion in polymers [26], based on a dynamic bond percolation theory (DBP) model. This model takes cognizance of the fact that ionic hopping can occur on time scales faster than typical reorganization times of the polymeric host, and that the

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Superdefects in Na β'' Alumina: Computer Simulation of Ionic Conductivity and Conduction Mechanisms

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Mobile-ion correlation phenomena in Na^+-β'' alumina are studied using the Monte-Carlo (MC) method to analyze a lattice hopping model of ionic behavior. Ionic conductivity is calculated for various ion-site occupancies, ρ's, and a wide range of temperatures. Significant curvature of the Arrhenius plot, which resembles certain experimental data on β'' aluminas, is found for $\rho = 0.5$. This observation is analyzed in terms of formation of a long-range ordered superlattice. The mechanism of charge transport on the superlattice involves movement of complex defects of the vacancy-type, which we call supervacancies, or of the interstitial-type, which we call superinterstitials. The Nernst-Einstein relation holds for superdefects. Finally, the optimum ion density for conduction is estimated for different temperatures.

I. Introduction

One particularly important and difficult issue in understanding mechanisms for motion of the mobile ions in framework ion conductors involves the role of ion-ion correlations in the conduction process [1-4]. Comes et al. [5] have shown from X-ray scattering investigations that ordering of the Na^+ ions and vacancies in the conduction slab of Na β'' alumina sets in at lower temperatures for compositions in which the site fraction, ρ, occupied by Na^+ is close to 0.50. Such studies have raised a number of questions about conduction mechanisms in such structures. (1) Over what range of ρ can ordering effects be observed? (2) What is the dependence of ionic conductivity on composition and on temperature in and near this range? (3) What is the optimal stoichiometry for maximum ionic conductivity? (4) What is the Na^+ ion conduction mechanism in such structures and how does the mechanism change as a function of ρ?

We have attempted to answer these questions by means of a computer simulation study of Na^+ ion conduction in β''-alumina as a function of temperature and crystal composition using the well-known Monte Carlo (MC) method [6-9]. Although this method suffers some disadvantages when compared with the molecular dynamics method for studying frequency-dependent conduction [10,11], nevertheless it has proved quite valuable in developing a better understanding of the d.c. conduction behavior in this class of compounds. Indeed, the pioneering MC studies of Murch and Thorn [7] on ion conduction in β and β'' aluminas have been especially helpful in elucidating the role of correlation effects on the conductivity of these materials. Other analytic schemes have also been devised for the investigation of ionic transport in framework conductors. In particular, Sato and Kikuchi [12-14] have developed a path-probability method (PPM) which is a type of cluster-variation method based on a kinetic form of the quasi-chemical approximation. Some discrepancies have arisen between the predictions of the MC method and those of the PPM for Naβ'' alumina, especially in the compositional region near $\rho = 0.50$; one goal of the present study is to clarify this discrepancy.

Perhaps the most interesting result of our study is the prediction of what we term "superdefects" (supervacancies and superinterstitials). At lower temperatures an ordered superlattice exists at the exact composition $\rho = 0.50$; then small deviations from the ideal composition $\rho = 0.50$ result in the introduction of interstitials or vacancies, which arrange themselves into "superdefects" on the superlattice. Such superdefects move quite readily and, indeed, appear to be the dominant mobile entities in the conduction process occurring in ordered phases of compositions near $\rho = 0.50$ at low temperatures.

II. Computation of Ionic Conductivity Using the MC Method.

The conduction plane in the β''-alumina structure is modeled as a two-dimensional honeycomb lattice in which all sites have the same potential for a single kind of mobile cation, and a vacancy mechanism for ion transport is assumed [16]. We choose the saddle-point energy for the Na^+ ions to be U, and assume that two Na^+ ions on nearest-neighbor sites interact repulsively with an energy ε. No interaction energy exists between a Na^+ ion and a NN vacant site or between two neighboring vacancies.

The ionic conductivity of our model for Naβ'' alumina is calculated from the Nernst-Einstein equation:

$$\frac{\sigma}{D_c} = \frac{q^2 C}{kT} , \tag{1}$$

where D_c is the charge diffusion coefficient, C

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Site Trapping and Commensurability Effects in Framework Solid Electrolytes

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We have performed Langevin dynamics calculations on a one-dimensional model for framework materials, focusing on the conductivity of interacting mobile ions in the presence of Coulombic traps. We observe several interesting phenomena, arising from competition among the three potentials (lattice, ion-ion, ion-trap). Findings of interest include: 1. Generally, the compensator will indeed trap a sufficient number of mobile ions to balance its charge. These ions can exchange, but they are quite well localized by the trap. 2. For incommensurate mobile-ion concentrations, the overall DC conductivity is decreased. 3. For commensurate concentrations, the DC conductivity can actually increase, as the trapping renders the remaining mobile-ion array effectively incommensurate.

I. Introduction

Framework solid electrolytes nearly always require disorder (high concentration of defects) on one sublattice for high conductivity to occur. Ordinarily, this is achieved by attaining a formally non-stoichiometric composition, such as $(Na_2O)_{1+x}\cdot 11Al_2O_3$ for β alumina. The concentration of mobile ions can often be varied by introduction of formally electrically-neutral components (such as Na_2O above) into the structure. If these are thought of as fully dissociated, then the carriers (Na^+) are accompanied by charge-compensating counterions ($O^=$), which remain in the structure, usually at rather clearly well-defined positions, and can therefore effect mobile ion motion in three ways: by distortion of the framework lattice, by blocking of pathways, and by Coulomb trapping. Theoretical studies [1] of ionic motion in framework electrolytes have largely ignored the effect of charge-compensating ions, and assumed either a simple lattice-site model or a simple periodic background due to the framework. The role of charge compensators has been studied by the Oak Ridge group, who present evidence for motions in the spinel block due to Coulombic forces [2], and more specifically by Wolf [3], who introduced a mechanistic transport model in which very strong trapping by compensators is invoked to discuss the temperature dependence of the Haven ratio.

More general considerations were presented long ago by Mott [4], the context of the metal-insulator transition. He argued that the Coulombic trapping, which is strong for low concentrations of charge carriers, will become screened as the carrier concentration increases, and that, when the screening length is of the same order as the lattice constant, the formerly trapped charges become free, and the (excitonic) insulator becomes conductive. Similar ideas seem reasonable for ionic materials, though the screening effect should be reduced somewhat; it should be more reminiscent of Debye-Hückel screening in liquid electrolytes [5]

Several charge compensation mechanisms have been postulated for non-stoichiometric ionic conductors. Three possible mechanisms for the compensation of excess cations are: 1) cations in the framework are replaced with cations of lower oxidation state. For example, in NASICON ($Na_3Zr_2PSi_2O_{12}$), the Na^+ ion concentration can be increased when the extra positive charge is balanced by replacing P^{+5} with Si^{+4} in the framework; 2) extra cations can be placed in the conduction region if there exists a corresponding number of cation defects in the framework; and 3) charge neutrality can be maintained if the excess cations are balanced by interstitial anions.

Trapping sites will be generated by these three charge compensation mechanisms if the deviations in the framework structure are localized near the conduction pathway. Trapping sites might also be created by impurities in the framework not associated with charge compensation.

Our objective, in the present paper, is to study the competing roles of ionic correlations, background periodic potentials and compensator trapping on the conductivity of a one-dimensional model for solid electrolytes. The method employed will be stochastic Langevin dynamics [6], which we have used previously [7,8] to examine the role of correlations on the frequency- and temperature-dependent conductivity of such materials. We find that there is an interesting trade-off among the three potentials in the problem, and that Coulombic trapping can, under special conditions, actually increase the conductivity.

The computations are performed for a one-dimensional model consisting of charged ionic carriers moving in a sinusoidal potential and subject to trapping by off-axis charge compen-

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DYNAMICS OF METAL ELECTRON EXCITATION IN ATOM–SURFACE COLLISIONS: A QUANTUM WAVE PACKET APPROACH

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Electron–hole pair excitations upon atom impact on a metal surface are studied in a framework of a one-dimensional independent-electron model. The method employed treats electron dynamics quantum mechanically and the atom motion classically, and the two are coupled through the time-dependent self-consistent field (TDSCF) approximation. A variational method is used to calculate the time evolution of the electronic wave packet. Calculations were carried out for the colliders, He, Ar and H; the surface parameters were chosen to model Li. Some of the results obtained are: (1) Electron excitation by H is much more efficient than for a rare-gas collider. Experimental search for hole-pair excitations should thus be best pursued with H as a collider. (2) At 0 K surface temperature $\Delta E/E$, the fraction of collision energy converted to hole-pair excitations, decreases as the collision energy increases for energies up to ~1 eV. At collision energy $E = 0.01$ eV, the fraction of energy transferred is ~0.2% for He and ~10% for H. (3) Atom trapping due to energy transfer to electrons occurs with high probability (50–100%) at sufficiently low collision energies. Ar trapping takes place at energies below 1 K and H trapping below 20 K. (4) The calculations show a pronounced transition from atom de-excitation to atom excitation by electron–hole pairs as surface temperature increases. (5) Perturbation theory is tested against the present method. It breaks down mainly for trapping and for temperature effects.

Abstract

A Monte Carlo method is developed for simulation of mixed ionic conductivity in β''-alumina-type materials. The conduction plane of these materials is represented by a lattice gas model in which monovalent and divalent cations carriers diffuse via a vacancy mechanism and interact through a nearest-neighbor Coulombic repulsion.

By comparing experimental data for pure Na^+ and pure Ba^{++} β''-aluminas with simulation results, it is possible to estimate the near-neighbor interaction energies ε_i and jump barriers U_i for both kinds of ions. On the basis of these estimations the total ionic conductivity of Na^+-Ba^{++} β''-alumina is calculated as a function of temperature and concentration of carriers. As Ba^{++} replaces Na^+, the conductivity initially increases as more vacancies become available. For very high temperatures, this increase continues until exchange is complete; but at lower temperatures, the conductivity reaches a peak for some optimal Ba^{++}/Na^+ composition, and then drops off as the number of Ba^{++}, and hence the strength of ionic correlation, goes up. The presence of ordering in the fully-exchanged (all Ba^{++}) case manifests itself in substantial curvature of the Arrhenius plots for conductivity. The activation energy for conductivity as a function of Ba^{++} mole fraction ($X_{Ba^{++}}$) shows a pronounced rise near an X value of 2/3, in agreement with recent experimental observations.