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13. ABSTRACT (Maximum 200 words) Work performed over the past six years is described. Studies have ranged over a variety of halide based materials (principally fluorides) in which the oxygen in oxide ferroelectrics is replaced by fluorine. For these systems, the use of free ion wavefunctions to calculate Gordon-Kim parameter-free modified electron gas potentials leads, overall, to good agreement with experiment and predicts the existence of ferroelectric phases for certain of these systems that have yet to be synthesized. We also have performed work on the oxide-based systems based on the potential-induced-breathing (PIB) model which permits spherical distortion of the O ²⁻ charge density. While this does not lead to ferroelectricity, it has a significant effect on the ferroelastic transitions associated with rotational instabilities of the oxygen octahedra. Finally, we have examined the effects of free surfaces on ferroelectric behavior and find them to be large.				
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**First Principles Theoretical Studies of
Ferroelectric Lattice Instabilities**

FINAL REPORT

Submitted to:

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Submitted by:

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Introduction

This program grew out of previous work aimed at understanding and producing materials with large optical constants (dispersion and loss) in the electromagnetic microwave region. Ferroelectrics showed promise in this area, particularly if their paraelectric-ferroelectric transition temperatures lie in the ambient region. We were able to explain this behavior as arising from ionic motions in the double-well potential which we now believe to be intrinsic to virtually all structural transformations in ionic insulators. However, only if this motion has a uniform polar component, i.e., is incipiently ferroelectric, can it couple directly to external electromagnetic radiation.

The basic thrust of the new program was to attempt to predict and explain ferroelectric behavior from first principles based primarily on the use of the local density approximation of which we employed the simplest, the Gordon-Kim modified electron gas technique.

Novel Halide-Based Systems

While the primary interest was in known ferroelectrics, i.e., oxide-based perovskites such as BaTiO_3 , our initial focus was on novel halide-based perovskites, one of which, NaCaF_3 , we had identified theoretically by employing Gordon-Kim potentials and molecular dynamics, to be a strong primary ferroelectric below $\sim 600\text{K}$. Since the pure compound has yet to be synthesized by standard techniques, we first began to study binary mixed fluorides in which NaCaF_3 is one component and the other is a fluoride which can be synthesized in its pure form: specifically, we chose first KCaF_3 and then NaMgF_3 .

The resultant studies are described in the following pair of abstracts:

Ferroelectrics, 1991, Vol. 120, pp. 143-155
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THE EFFECT OF K DEFECT CLUSTERS ON THE FERROELECTRIC PHASE TRANSITIONS IN NaCaF_3

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(Received March 6, 1991; in final form June 29, 1991)

We have performed a number of molecular dynamics computations on 320 ion samples of NaCaF_3 containing K substitutional defects in various concentrations and configurations. *Ab initio* potentials with no adjustable parameters were used to obtain the short range interactions between ion pairs. Our results indicate that the presence of these defects, in most cases has a profound effect on the characteristics of the polar state, including a diminished sharpness of the transition temperature. We believe that these results may lend some insight into the mechanisms which produce "relaxor" ferroelectrics.

Keywords: ferroelectrics, perovskites, molecular dynamics, defects

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DIFFUSIVE PHASE TRANSITIONS IN MIXED HALIDE FERROELECTRICS

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(Received March 6, 1992; in final form June 22, 1992)

Molecular dynamics simulations have been performed for the $\text{NaMg}_{1-x}\text{Ca}_x\text{F}_3$ materials where Ca ions were substituted for Mg in NaMgF_3 in varying concentrations of randomly distributed defects representing constitutional crossover. Small clusters of Ca defects in NaMgF_3 and clusters of Mg defects in NaCaF_3 were also studied. First-principles calculations were used to calculate the potentials between ion pairs in these samples. The change of defect concentration results in a gradual shift from nonferroelectric behavior of NaMgF_3 to ferroelectric behavior of NaCaF_3 . Doping in these materials leads to a "smeared out" transition "range" instead of a sharp transition temperature—the so-called diffusive transition.

Keywords: diffusive phase transition, perovskite

While ferroelectric halide perovskites have yet to be fabricated, other systems, notably BaMgF₄, do show polar phases; moreover, the polarity is "switchable" by an external field.

We, therefore, initiated and carried through a fairly extensive study on these systems which is described in the following pair of abstracts:

Ferroelectrics, 1994, Vol. 153, pp. 67-72
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MOLECULAR DYNAMICS SIMULATION OF BaMgF₄ and BaMnF₄

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(Received August 9, 1993)

Abstract We have performed molecular dynamics simulations on BaMgF₄ and BaMnF₄, both of which have been reported to have polar structures, with T_c above the melting point. We have determined the ground state structure and verified the polarization mechanism described by Keve *et al.*¹. Polarizations of 8.5 $\mu\text{C}/\text{cm}^2$ are found for the Mg compound at 0 K and 11.7 $\mu\text{C}/\text{cm}^2$ for the Mn compound. We find no indication of ferroelectric phase transitions between 0 K and 1200 K for either material. We are able to reverse the polarization of the Mg compound by simulating a external field, while the Mn based material distorts, but does not reverse polarity. We have simulated substitutions of Be for Mg and Mn in these materials. We report on these results.

Molecular-dynamics simulations of some BaXF_4 compounds

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(Received 21 September 1993)

We have carried out molecular-dynamics simulations on BaXF_4 compounds, where X is Mg, Mn, or Zn. *Ab initio* potentials, with no adjustable parameters, were used to obtain short-range interactions between ion pairs. We found a polar ground-state structure which is in agreement with the $A2_{cm}$ space group reported experimentally. We were able to reverse polarization in BaMgF_4 at high temperatures, using large fields, but were unable to reverse polarization in the other compounds. The second-order phase transition in the Mn compound at 250 K was reproduced. We believe this to be the first extension of molecular dynamics to materials consisting of chains of F octahedra.

While we have subsequently, using State of Nebraska Research Initiative and funding under the NSF EPSCoR program, attempted to synthesize some of these mixtures experimentally, we have found that if Na^+ is present, it is segregated as NaF together with similarly segregated CaF_2 .

Oxide Ferroelectrics

In parallel with this work on halides, we finalized and made specific our work on the dielectric properties of linear double well systems by applying it to SbSI. This is summarized in the following abstract:

A DOUBLE WELL OSCILLATOR MODEL FOR THE FERROELECTRIC PHASE TRANSITION IN SbSI

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(Received December 17, 1991)

The dielectric response spectrum for antimony sulfide has been computed using a model in which the material is simulated by a damped double well oscillator. It is found that with the use of simple damping and relaxation terms and realistic well parameters the experimental dielectric response, including the central peak, can be reproduced quite closely. The choice of well depth, in particular, plays a major role in determining the frequency of the first peak above the soft mode.

As the work by other groups funded under this program progressed, it produced a disturbing anomaly. While their local density approximation LAPW total energy calculations could produce double-well ferroelectric structures for BaTiO₃ etc., this was only true if the experimental lattice constants were imposed. At the exact theoretical volume, that of minimum static energy, the minima were either absent or implausibly shallow.

This raised the question of how valid *any* calculation which imposes periodic boundary conditions was for a ferroelectric, owing to the infinite-range effects associated with plane polar surfaces.

We thus made a specific study of this question using a system of NaNO₂ molecular ions. The results, described in the abstract below, indicate that this is a genuine problem (whether or not it influences the double wells in BaTiO₃ and other oxide perovskites), and its understanding is of serious practical importance in the context of thin-film ferroelectric memories.

FERROELECTRIC TRANSITIONS, MOLECULAR DYNAMICS AND INTRINSIC SURFACE PROBLEMS

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(Received March 6, 1992; in final form June 25, 1992)

Conventional supercell molecular dynamics, if applied to a system where one has reasonable potentials and which is known experimentally to have a ferroelectric ground state, can fail to reproduce that state. We shall show that such behavior stems from a failure, intrinsic in this type of molecular dynamics, to handle the surface effects intrinsic to Coulomb interactions. We will discuss how this limitation can be addressed and its possible implication for ground state energies calculated by using periodic boundary conditions.

Keywords: ferroelectrics, supercell MD

While we were carrying out our studies on non-oxide-based systems, we were continually developing, in conjunction with Dr. Boyer at the Naval Research Laboratory, extensions and applications of the PIB (potential induced breathing) model, which represented an early attempt to study oxides allowing for the major effects of O^{2-} charge distortions on the potential energy surfaces for all oxide-based systems: notably, ferroelectric perovskites.

Unfortunately, this had only been carried to the point of determining the effect of PIB on rotational (nonpolar) instabilities, and developing a PIB-inclusive molecular dynamics program when funding was terminated.

Three specific studies are described in the following abstracts, the last representing our definitive results within the PIB limitations:

MOLECULAR DYNAMICS SIMULATION OF THE PHASE TRANSITION IN LaAlO_3

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(Received August 9, 1993)

Abstract We have used molecular dynamics and lattice statics to study LaAlO_3 in the temperature range 0 - 1500 K. Short range pair potentials were obtained using the Gordon-Kim¹ approach. The O^{2-} ion charge density was stabilized using Watson Sphere potentials ranging from 0.7 to 0.8 Har./e. within this range, a phase transition is found to occur at the temperature reported experimentally (800K), however, we find the ground state to have a tetragonal (Pmnb) structure rather than the observed $\text{R}\bar{3}\text{C}$ configuration. It is found that the $\text{R}\bar{3}\text{C}$ structure can be stabilized by transferring charge from the O^{2-} ion to the La^{+3} ion in the long range potential sums.

A STUDY OF THE STRUCTURE AND STABILITY OF SrCuO_2

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(Received August 9, 1993)

Abstract We have investigated the structure and stability of SrCuO_2 using both lattice statics and dynamics techniques as well as molecular dynamics. Short range interatomic pair potentials were obtained using Gordon-Kim¹ techniques. Lattice dynamics indicates that the infinite layer, high T_c parent structure of Azuma *et. al.*² should not be stable for this material, with the largest instabilities appearing in the plane perpendicular to the Cu-Cu bonds (i.e. in the ab plane). The ground state structure and temperature variation of physical parameters obtained from molecular dynamics simulations will be discussed, as will the effects of varying ionicity.

INTERPLAY OF IONIC BREATHING AND ROTATIONAL INSTABILITIES IN PEROVSKITES*

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(Received April 1, 1994; in final form June 20, 1994)

In a previous work¹ we have used parameter-free potentials, developed by the Gordon-Kim technique, to study rotational instabilities in halides-based perovskites by molecular dynamics. These calculations assumed rigid spherical ions unchanged by incorporation in the crystals. We have now extended this approach to include the potential-induced breathing (PIB)² associated with purely radial distortions in the ionic charge densities induced by the electrostatic Madelung field in the lattice. In addition we have examined the effects of using different forms of density functionals³ in the Gordon-Kim potentials. Results will be presented for both halides-based and oxygen-based perovskites.

Keywords: Molecular dynamics, Gordon-Kim potentials, perovskites

However, Dr. Boyer has since made major progress with generalizations of the PIB approach, and we are currently continuing this collaboration with local funding.