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Preliminary work on the theoretical understanding of polar (ferroelectric) lattice instabilities in ceramic oxides is described. Emphasis is placed on the need to handle electronic charge density redistribution and its effects on lattice instabilities. The emphasis is on doing so with as few variables as possible in order to make molecular dynamics studies of phase stability and other properties possible. In addition, a summary is presented of work carried out to "round out" studies under our previous ONR Award.			
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Work on this new program was effectively initiated in April/May, and the body of this report will mainly be concerned with new initiatives and completion of earlier ONR funded work.

While no definite conclusions have yet been reached, the basic nature of the problems to be studied has been defined.

A. Goals

The objective of this new program can be stated very simply; it is to incorporate the effects of electronic charge redistribution into calculations of changes in lattice potential energies for arbitrary crystal distortion and thus to predict its influence on the uniform polar (antiphase motion of positive and negative ions) distortions associated with ferroelectricity in oxide based ferroelectrics.

Our belief that this is central to the understanding of ferroelectric behavior in these, the overwhelming majority of such materials, is based on earlier studies during the previous program. These demonstrated two basic facts: (a) Theoretical Studies on halide based perovskites revealed that some of these; e.g., NaCaF_3 , can show ferroelectric behavior purely due to ionic "size" effects (electronic polarization is secondary due to the small polarizability of the F^- ion). However, this transformation occurs because the Na^+ and Ca^{2+} are approximately equal in size and, unfortunately, this condition apparently precludes the existence of NaCaF_3 as an equilibrium phase under ambient pressure. (b) Similar theoretical investigations of BaTiO_3 revealed no ferroelectric instability: certainly, the widely disparate sizes of Ba^{2+} and Ti^{4+} rules out behavior similar to that of NaCaF_3 . Furthermore, the most obvious other possibility, that Ti^{4+} is so small that it "rattles" inside its octahedral "cage" of six oxygens is again ruled out since the ionic radii are such that Ti^{4+} and O^{2-} come into contact marginally before adjacent pairs of O^{2-} ions overlap. Again, one suspects that attempts to reverse this by using different ions could well render the perovskite phase thermodynamically unstable.

Evidently, there is something missing in the description of the oxide based systems and the obvious candidate is electron redistribution.

However, it has been known for ~ 50 years that attempts to approximate this by point dipoles at the ion centers produces completely unphysical results, even in the simplest systems, e.g., the heavier sodium halides are no longer stable in the rocksalt structure. Furthermore, one also has to explain why BaTiO_3 is strongly ferroelectric while SrTiO_3 is only on the verge of being polar.

Very recent NRL work based on LAPW total energy calculations does predict a ferroelectric ground state for BaTiO_3 but has not clearly defined the origin of this behavior, apart from indicating that charge transfer from the O^{2-} ions into the unfilled d states of Ti^{4+} plays a significant

role. Unfortunately, such studies are extremely time consuming, and offer no hope of providing the type of potential function that we have obtained from Gordon-Kim rigid ion calculations for halide based systems. Clearly incorporation of electron redistribution effects effectively increases the number of degrees of freedom per ion, but this can be handled if this redistribution can be characterized by a relatively small number of parameters. An example, is the point dipole approximation, alluded to earlier. Evidently, this is a very bad approximation; but it does completely characterize the charge redistribution using only three additional degrees of freedom per ion. It is clearly implausible that any description can have fewer parameters, but it does not necessarily follow that any triplet of parameters will be equally bad.

Currently, a sequence of LAPW calculations has been initiated at NRL designed to examine in detail the nature of the charge distortions in BaTiO_3 associated with polar motion. The first objective is to determine the best representation of the charge distribution in terms still of purely spherical ions. Then the next stage will be to isolate the regions in which the fit is worst and then to further reduce the discrepancy by introducing new spherical distributions away from the ion centers.

B. Results

Initiation of New Work

The optimized spherical distributions alluded to in the previous section were derived at NRL using the "Potential Induced Breathing" (PIB) model. As a first stage in the present study, Professor J. W. Flocken has been applying this to LaAlO_3 in order to see if we can correctly reproduce the cell multiplying transition in that system. Results thus far indicate considerable sensitivity to the manner in which the O^{2-} ion is stabilized in PIB.

Dr. H. M. Lu has been studying the dynamics of ionic molecular systems when one simulates polarization effects by permitting rigid displacement of the valence electrons with respect to the core but uses *a priori* potentials for the various interactions. This work is ongoing and could well be generalized to introduce other spherical charge distributions not centered on the ions.

Professor R. A. Guenther has begun extending to two dimensions the theory of the dielectric response of double-well systems, which was central to our understanding of dielectric loss in SbSI under the previous Award.

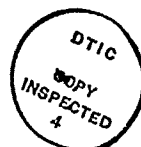
Professor J. W. Flocken and Dr. Z Mo have been completing their studies on mixed halide perovskites; specifically, the $(\text{Na}, \text{K}) \text{CaF}_3$ system. Since (non-ferroelectric) KCaF_3 can be grown,

we wish to discover what level of Na substitution is needed to initiate the ferroelectric behavior predicted theoretically for NaCaF₃ since, if this is low enough, it should be possible to produce such systems by doping pure KCaF₃.

The three graduate students who have begun work since the initiation of the new program are principally acquiring familiarity with our existing codes and molecular dynamics capabilities. They are also learning the basic theory underlying these tools. This provides an opportunity for them to begin exploratory studies on the general problem of obtaining accurate representation of electron charge distribution with a minimal number of parameters.

C. Future Work

During the coming year, work on the topics just described will be continued with particular emphasis uniting the NRL studies on LAPW charge densities with our work on representing these densities and variations with minimal numbers of parameters determined by self-consistency. It is possible that other topics may emerge as priorities thus dictating new areas of emphasis; however in view of the limited duration of the present program to date, it would be unwise at this stage to instance specific possibilities.



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D. List of Publications/Reports/Presentations

1. Papers Published in Refereed Journals

J.W. Flocken, W.N. Mei, R.A. Guenther, J.R. Hardy, P.J. Edwardson and L. Boyer, "Ferroelectric Phase Transitions in Na-Ca-Halide Perovskites," *Ferroelectrics*, 10, 411 (1990).

H.M. Lu and J.R. Hardy, "Ab initio Simulations of Phase Transitions in KNO_3 ," *Ferroelectrics*, 111, 43 (1990).

J.W. Flocken, W.N. Mei, R.A. Guenther, J.R. Hardy, and L.L. Boyer "Ferroelectric Phase Transitions in Mixed Na,K-halide Perovskites," *Phase Transitions*, 20, 113 (1990).

2. Non-Refereed Publications and Published Technical Reports

None.

3. Presentations

a. Invited

J. W. Flocken, J.R. Hardy, and H.M. Lu, "Lattice Anharmonicity and High T_c ," University of Miami Workshop, January 1991.

b. Contributed

J.R. Hardy and J.W. Flocken, "Anomalous Isotopic Shifts and Vibronic Theories of High T_c ," *Bull. Am. Phys. Soc.*, 35, 291 (1990).

J.W. Flocken, R.A. Guenther, and J.R. Hardy, "Simulation of the Central Peak in Linear Ferroelectrics Using a Double Well Potential," *Bull. Am. Phys. Soc.*, 35, 541 (1990).

H.M. Lu and J.R. Hardy, "First-Principles Studies of Phase Transition in KNO_3 ," *Bull. Am. Phys. Soc.*, 35, 542 (1990).

4. Books (and sections thereof)

None.

Enclosure (2)

E. LIST OF HONORS/AWARDS

<u>Name of Person Receiving Award</u>	<u>Recipient's Institution</u>	<u>Name, Sponsor and Purpose of Award</u>
Q. Rui	U. of Nebr.	Avery Fellowship Summer 1991
Q. Rui	U. of Nebr.	Buckey Fellowship Fall 1991 - Summer 1992

Enclosure (3)

F. Participants and their status.

J.R. Hardy, P.I., 1 month summer, 1/5 AY

J. W. Flocken, Faculty Associate, 2 months summer

H.M. Liu, Postdoctoral, 25% CY

Q. Rui*, Graduate Student, 25%

H. Cao, Graduate Student, 25%

M. Ossowski, Graduate Student, 50%

In addition to these foregoing personnel, Professor R. A. Guenther and Dr. Z. Mo also participate in the program but were supported entirely by State of Nebraska funds.

*During the past year Ms. Rui has been awarded two UNL Fellowships: Avery Fellowship (Summer 1991) and Buckey Fellowship (Fall 1991 and Summer 1992).

G. Other sponsored research during FY '90.

ARO - Award \$100 K, Oct. '90 - Sept. '91, P.I. supported 2 months summer, 1 month AY.