

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

AD-A210 143

1a. REPORT SECURITY CLASSIFICATION		1b. RESTRICTIVE MARKINGS 77C FILE COPY	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		4. PERFORMING ORGANIZATION REPORT NUMBER(S)	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR-89-0875	
6a. NAME OF PERFORMING ORGANIZATION University of Georgia Athens GA 30602	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION AFOSR	
6c. ADDRESS (City, State, and ZIP Code)		7b. ADDRESS (City, State, and ZIP Code) BLDG 410 BAFB DC 20332-6448	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION AFOSR	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR 76-3045	
6c. ADDRESS (City, State, and ZIP Code) BLDG 410 BAFB DC 20332-6448		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO. 61102F	TASK NO. B2
		PROJECT NO. 2305	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) BAND CALCULATIONS ON FERROELECTRIC AND PIEZOELECTRIC SOLIDS			
12. PERSONAL AUTHOR(S) J.H. Henkel, C.A. Uzes, M.H. Lee			
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) Jan 1979	15. PAGE COUNT 11
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code) 767-4984	22c. OFFICE SYMBOL NE

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AFOSR-TR- 89-0875

FINAL
~~ANNUAL~~ REPORT

Grant AFOSR 76-3045

1 June 1977 - 1 October 1978

BAND CALCULATIONS ON FERROELECTRIC AND PIEZOELECTRIC SOLIDS

by

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DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/ _____	
Availability Codes	
Dist	Avail and/or Special
A-1	

The main objectives of the original proposal were to calculate spontaneous and other polarization properties of polar and piezoelectric crystals. The purpose of the work was to aid in selecting the best pyroelectric materials to be used in pyroelectric image tubes. The crystals for which the main work effort was directed were: NaNbO_2 , BN , LiNbO_3 and KNbO_3 . Calculations on the first three crystals have led to five publications and calculations on the last are being compiled for publication. Publications on other aspects of the grant are listed in the List of Publications which includes the five publications mentioned above.

The computer program used to make the calculations was written by R. N. Euwema formerly at the Aerospace Research Laboratory, WPAFB, Ohio. Using charge densities obtained from band calculations with this program, the following piezoelectric coefficients d_{21} , d_{22} , and d_{23} for sodium nitrite have been calculated. This was accomplished by calculating the changes in the electric polarization of sodium nitride for three different strains. The piezoelectric coefficients are linear relations relating induced polarizations to applied stresses. Experimental elastic coefficients were used to obtain stresses from the above strains. There are some uncertainties in the experimental elastic coefficients C_{13} and C_{23} . The uncertainties

in the coefficients C_{13} and C_{23} give rise to uncertainties in the piezoelectric coefficients d_{21} and d_{23} . Our calculated value for the piezoelectric coefficient d_{22} compares well with the experimental value while the calculated values of d_{21} and d_{23} agree only fairly well with experimental values. The details of the calculations and the results of the calculations are presented in the article of reference (2).

Nonlinear strain - polarization calculations were made on crystalline NaNO_2 . These calculations showed a dependence of polarization of strain that had a discontinuous slope. A short article on a possible second order phase transition in crystalline NaNO_2 due to strain is to be published in Physics Letters.

The plain-wave-Gaussian mixed basis method has been employed to calculate crystalline energy bands for cubic boron nitride (zinc-blende structure). These calculations agree favorably with experiment. Polarization calculations for sheared piezoelectric cubic boron nitride have been undertaken. With a shear strain $\epsilon_4 = .001$ along the boron-nitrogen bond which is directed along the body diagonal in the unit cell, the polarization is changed about -9.56×10^3 e.s.u./cm². In order to calculate the corresponding piezoelectric constant the stiffness constants for boron nitride are needed. So far these have not been found. However, they can be estimated to determine piezoelectric coefficients.

The spontaneous polarization of LiNbO_3 has been calculated and the value differs by 20 percent from the experimental value. Because LiNbO_3 contains so many electrons in a unit cell we were not able to do a thorough calculation on LiNbO_3 as was done on NaNbO_3 .

The article entitled "Off-Diagonal Disorder in Dilute Alloys" has been published in Physical Review B. The research on the work was sponsored in part by the grant. The content of the paper is to resolve the difference between the results of Fukuyama, Krakauer, Schwartz and Hwang and Sher on the electronic density of states in dilute metal alloys with off-diagonal disorder retained in the Hamiltonian. The work is accomplished by introducing an alternative decomposition of the alloy Hamiltonian in the Hwang and Sher formalism.

The Operator Recursion Method was previously applied to the motion of a single particle moving in a 1-dimensional periodic lattice. Work on the method in this final year of the grant involved its extension to 3-spatial dimensions and to the many body problem. The previous cumbersome procedure of the self-consistent removal of momentum operators from the recursion equations has been replaced by a generating function technique ^{A,B}. The recursion relations are now developed around a matrix element of products of a periodic functions of position with powers of the momentum

operator. The recursion relation has been transformed into a linear partial differential equation for the generating function having a number of independent variables equal to the number of degrees of freedom, plus time. The charge density for the system is determined by the initial conditions of the generating function, while the band structure follows from separating out the time variable and solving the associated eigenvalue problems. The problem of the separation of variables is mitigated by group theoretical results following from the symmetries of the system.

The generating function procedure is also employed in approaching the many body problem. Here the recursion relation is developed for matrix elements of normal products of raising and lowering operators. For a 1-dimensional system involving only coupling between the "charge" density with an external potential the generating function involves 3 time and 2 additional independent variables. Again the band structure and charge density follow from the separation of variables and the linear PDE initial conditions. More complicated systems involving self coupling of the field lead to an increase in the number of independent variables, the number being a function of the number of degrees of freedom. Relaxation of the system is described by solutions of the PDE which are associated with non-self adjoint operators acting on the generating function. Investigations are continuing on the classification and application of these equations.

The interaction of a ferro or pyroelectric system with an external field in the dipole approximation was previously described (in our Proposal 1977). The polarization relaxation function describes how such a system responds to an external perturbation. It is also essential for calculating other time-dependent properties of ferro and pyroelectric materials. Taking advantage of the two recent methods developed by us, we have calculated the relaxation function for a van der Waals charge system. A charge density system, e.g., a ferroelectric material, where all charges interact with all others with equal strength is called a van der Waals charge system. Although this model system greatly simplifies many complexities of real systems, it is now known that this model treats static and dynamic properties sensibly as long as the systems are not in the critical region.

The relaxation function is defined by

$$R(t) = Z^{-1} \text{Tr}\{e^{-\beta H} P(t) P\}$$

where Z is the partition function, P is the charge density operator. Using the van der Waals charge model for H , we have deduced analytic expressions for $R(t)$ in different spatial symmetry regimes. (Previously we had obtained only leading factors. We now have complete solutions.) The

spatial symmetry enters into the problem through spatial orientation of the interaction given in H. If the interaction is spatially random, one has a Heisenberg-like rotational symmetry. If the interaction is dominantly planar, one has an XY-like rotator symmetry. If the interaction is linear, one has an Ising-like asymmetry. We have now obtained exact solutions for a number of pure symmetries and mixed symmetries.

Here we shall summarize our results which will appear in Physical Review 1979. Our general results fall into two physical regimes: above and below the transition temperature. If temperature is above the transition temperature, the relaxation function is exactly Gaussian for both the linear and planar spatial symmetries,

$$R(t) = R(0) \exp-(At)^2$$

where

$$R(0) = \langle P^2 \rangle .$$

The relaxation function for the rotational symmetric case is uninteresting as it vanishes with the vanishing of the perturbation. This arises from random orientation of interaction which does not discriminate the manner in which it is perturbed. For the other pure symmetric cases, the widths of the Gaussian A^{-1} are of importance. For the

planar spatial symmetry, the width is constant, not depending on temperature. Hence, the relaxation function "dies" very smoothly in time unaffected by fluctuations in charge densities brought about by thermal energies. For the pure linear spatial symmetry, the width is temperature-dependent. Hence, the relaxation function for this case does not behave monotonically. As the temperature is lowered toward the critical temperature for example, there is narrowing of the width resulting in critical slow down of all relaxation processes.

If temperature falls below the transition temperature, the shape of the relaxation function now becomes dependent on the nature of spatial symmetries directly. For the pure planar spatial symmetry the relaxation function shape remains Gaussian whose width, however, is no longer temperature-independent. It has a $T^{-1/2}$ -dependence in such a way that it grows significantly with temperature. For the pure linear spatial symmetry, the relaxation function is oscillatory,

$$R(t) = R(0)\cos \omega t + Q(0) \sin \omega t,$$

where Q is to a leading order a time independent constant depending on temperature, the frequency is a precessional frequency depending on the degree of internal ordering. It vanishes, for example, at the critical temperature

suffering critical slow down.

The advantage of using the van der Waals model for complex systems becomes apparent from these solutions, in particular from the correspondence we have established for one dimensional problems. In the high temperature limit (i.e., $T \rightarrow \infty$), numerical and analytical solutions for 1-dimensional nearest-neighbor interaction model indicate that $R(t) \sim \exp(-J^2 t^2)$, where J is the strength of the nearest neighbor charge coupling. This result is directly obtainable from our van der Waals solutions if one properly adjusts the range of interaction in the H used for the van der Waals model. Thus, even for highly complex ferro and pyroelectric materials, their time-dependent behavior is qualitatively correctly described by the van der Waals model. (Establishing this result was the main purpose of this phase of our proposed work). For quantitative accuracy one must forgo the analytic approach and utilize high-speed computers. This may be done by adding to the van der Waals mode some additional features of interaction but preserving the spatial symmetries. These results and their applications to other dynamical problems have been reported at a recent international physics conference held in Grenoble France. The details of this contribution will appear in the Journal de Physique (Paris).

List of Publications

- (1). "Polarization Calculations For Ferroelectric Sodium Nitrite," J. H. Henkel, T. C. Collins, J. L. Ivey, and R. N. Euwema, International Journal of Quantum Chemistry Symp. No. 9, 529-533 (1975).
- (2). "The Calculated Polarization and Piezoèlectric Constant of NaNO_2 ," Kam-Shing Kam and John H. Henkel, Phys. Rev. B17, #3, 1361-1364 (1978).
- (3). "Energy Band and Piezoelectric Calculation on Cubic Boron Nitride," Hsing-chow Hwang and John H. Henkel, Phys. Rev. B17, 4100-4103 (1978).
- (4). "Band Structure and Spontaneous Polarization of Ferroelectric LiNbO_3 ," Kam-Shing Kam, John H. Henkel, Hsing-chow Hwang, J. of Chem. Physics 69(5), 1949-1951 (1978).
- (5). "Possible Second-order Phase Transition of Ferroelectric NaNO_2 Produced by Strain," Kam-Shing Kam and John H. Henkel, Physics Letts A, (accepted for publication).
- (6). "Off-Diagonal Disorder in Dilute Metal Alloys," Phys. Rev. B16, 3840-3844 (1977).