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STATISTICAL-MECHANICAL STUDY OF POLYVINYLIDENE FLUORIDE
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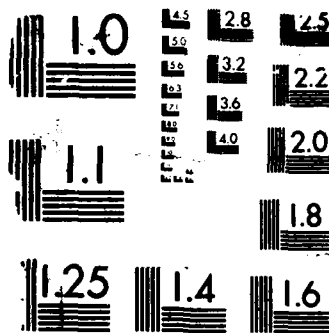
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STATISTICAL-MECHANICAL STUDY OF POLYVINYLIDENE FLUORIDE

FINAL REPORT

PHILIP L. TAYLOR

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U.S. ARMY RESEARCH OFFICE

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <i>Be to</i> A theoretical study of polyvinylidene fluoride has been performed in which calculations have been made of the equation of state, of the piezoelectric and pyroelectric coefficients, and of the mechanism of poling of β phase material. Transfer integral and mean-field methods have been used to derive the free energies of the various phases, and thence to derive the thermodynamic variables as functions of temperature, stress, and applied electric field. The effect of lattice distortions on the		

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piezoelectric coefficients has been studied, with particular attention paid to the nonlinear coefficients and their origin. Other work includes study of polyvinylidene fluoride as a detector of energetic heavy nuclei and investigation of the properties of random copolymers.

(Keywords) →

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A. Statement of the Problem Studied

The performed research consisted of a theoretical study of both equilibrium and non-equilibrium properties of poly(vinylidene fluoride), hereafter referred to as PVF_2 . This material can exhibit strong piezoelectric and pyroelectric effects if suitably prepared, and is consequently of great technological interest. The study consisted of a series of calculations of the equation of state, and the mechanism by which electrical activity is induced.

Detailed accounts of the results of our investigations have been given in the papers listed in section C, and so we here just provide a brief summary of some of the more important aspects of our work.

B. Summary of Most Important Results

Polyvinylidene fluoride is a remarkable material in that it can be produced in a form in which it has a spontaneous electric dipole moment. Unlike ceramic ferroelectrics, in which the moment arises from an instability in the phonon spectrum of a non-polar material, PVF_2 consists of a flexible chain composed of units of fixed dipole moment of about 7×10^{-30} coulomb-meters. The particular phase in which PVF_2 shows these effects is known as the β phase. We have made both analytical and numerical studies of the processes by which the piezoelectrical activity occurs, and have sought mechanisms for enhancing its magnitude and stability.

In one piece of work we have conjectured that the recently observed stress-induced variation in one of the piezoelectric coefficients of β -poly(vinylidene fluoride) may be due to an instability of the crystal lattice at modest strains. This instability arises as a consequence of the similiarity of the Bravais lattice to hexagonal form for the following reasons.

Typical samples of PVF_2 are in the form of films a few tens of microns thick, and of the order of 1 cm in width. These films are commonly first prepared in the α phase, and upon drawing the film at a modestly elevated temperature to a draw ratio of 4, a transition is realized from the α to the β phase. In the β phase of PVF_2 , a crystallite is characterized by a permanent polarization, but the polarization direction of different crystallites varies sufficiently that the film as a whole does not have a net polarization. Upon the application of an electric field of the order of 100 MV/m, a process known as poling, the polarizations of the crystallites are thought to reorient so as to point in directions close to that of the applied field, and this yields a typical net polarization of 0.05 C/m^2 .

Because of the absence of six-fold symmetry in the β - PVF_2 chain, there is no reason for the Bravais lattice to have precisely the dimensions of a perfect hexagon. We suppose that the equilibrium structure departs from pseudo-hexagonal by some small strain in the prolate direction, as has been reported experimentally. The energy as a function of this distortional strain would then have a minimum at the equilibrium dimensions. If each chain were now to be rotated by 60° the energy would vary with strain in such a way that the original structure could be recovered only by a new distortion of the lattice. Detailed energy calculations indicate that this is most likely to be the origin of the observed non-linearities.

In another piece of work the approximations made by previous workers in modeling PVF_2 were analyzed. This calculation indicated the sensitivity of the predicted polarization of a crystal of polarizable molecules to

the detailed assumptions made in formulating the model. It was shown that the Lorentz factor was strongly dependent on whether the finite size of the molecular electric dipoles is taken into account. It was also seen that, although the Lorentz factor itself may be negligibly small, its derivatives with respect to the lattice constants are not, and they significantly contribute to the piezoelectric and pyroelectric coefficients.

One interesting piece of work involved the interpretation of the reported use of PVF_2 to detect individual heavy nuclei of high kinetic energy. A mechanism had been suggested whereby an incident nucleus transfers to the sample an energy which appears as a heat pulse along the particle trajectory and spreads by heat conduction throughout the sample. The pyroelectricity of PVF_2 then produces charge on surface electrodes. We pointed out that another contribution to the measured charge, namely the irreversible depolarization through melting of the material in a cylinder of radius ~ 12 nm about the particle trajectory, could occur. This increases the initial sensitivity of the detector, but ultimately causes the device to be degraded.

Finally, it has been found that in random copolymers of PVF_2 with trifluoroethylene, the disorder present may make the poling process more rapid, but may reduce stability.

C. Publications Supported

1. R. Al-Jishi and P. L. Taylor, "Field Sums for Extended Dipoles in Ferroelectric Polymers," *J. Appl. Phys.* 57, 897 (1985).

2. R. Al-Jishi and P. L. Taylor, "Equilibrium Polarization and Piezoelectric and Pyroelectric Coefficients in Polyvinylidene Fluoride," *J. Appl. Phys.* 57, 902 (1985).

3. P. L. Taylor, "Relaxation in Crystalline Polymers," in Relaxation in Complex Systems, edited by K. L. Ngai and G. B. Wright (U. S. Dept. of Commerce, Springfield, VA., 1985).

4. R. Al-Jishi, L. L. Foldy, R. G. Petschek and P. L. Taylor, "Pyroelectric Materials as Electronic Pulse Detectors of Ultraheavy Nuclei," Phys. Rev. Letters 54, 1089 (1985).

5. P. L. Taylor, "Phase Transitions in Crystalline Polymers," Materials Science Forum 4, 105 (1985).

6. R. Al-Jishi and P. L. Taylor, "Possible Explanation for the Non-Linear Piezoelectric Response of Poly(Vinylidene Fluoride)," Ferroelectrics Letters 5, 1 (1985).

7. R. A. Al-Jishi and P. L. Taylor, "Influence of Electrostatic Interactions on Switching Characteristics in Poly(Vinylidene Fluoride)," Ferroelectrics, 73, 343 (1987).

8. P. L. Taylor, "Introduction to Polymer Ferroelectrics" Ferroelectrics 73, 331 (1987).

D. Participating Scientific Personnel

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V. K. Pinus, Research Associate

R. A. Al-Jishi, Research Associate

L. Huang, Graduate Assistant (M.S. earned 1986, Ph.D. expected 1988)

J. Wang, Graduate Assistant (no degree earned)

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