Ferroelectricity at General Motors Research Laboratories

Recent emphasis in research on ferroelectricity and lattice dynamics at General Motors Research Laboratories created the atmosphere for a symposium covering the theory of the phenomena and the search for new ferroelectric materials. The general and fundamental discussion was particularly enhanced by the presence of solid-state theorists such as John C. Slater, Herbert Fröhlich, Lars Onsager, David Pines and Roger J. Elliott. While recalling existing theories and discussing the present state of knowledge, the symposium opened new ways of further development. The symposium was held at GM, 19–21 Sept. 1966, in Warren, Michigan.

In the opening address, Slater gave an introduction to the theory of ferroelectricity reminding us that the permanent electric polarization is thought of in terms of displacement of the whole structure of positive ions with respect to the negative ones and that this polarization disappears at a critical temperature.

It has been emphasized that an essential difference exists in the behavior of two types of ferroelectrics, namely potassium dihydrogen phosphate, KH_2PO_4, and barium titanate, $BaTiO_3$. The difference resides in the magnitude of entropy increase in going through the critical temperature. In KH_2PO_4 the specific heat shows a large anomaly of the lambda-point variety at the critical temperature, whereas in $BaTiO_3$ the specific-heat anomaly is very small. No simple explanation has been given for this anomalous behavior.

Considering the dynamical properties of the system, namely the oscillatory motion of the positive and negative ions executing displacements out of phase, one finds a resonant frequency associated with this particular mode of vibration that vanishes at the critical temperature. This has been interpreted as a result of the Lorentz correction: the effect of long-range electrostatic forces resulting from the polarization itself, modifying and tending to cancel the short-range forces that arise from the attraction and repulsion between neighboring ions.

Fröhlich also emphasized the role played by the long-range Coulomb forces in the theory of dielectric properties of materials. He has shown that quite a number of features can be discussed in a macroscopic phenomenological way.

Nearly 20 years ago in the first edition of his book on dielectrics, Fröhlich pointed out that the approach to the critical temperature T_c from high temperature is often characterized by a very large static dielectric constant. This condition necessarily implies that in ionic crystals with a single optically active mode, the frequency ω_t of this normal mode vanishes as one approaches the ferroelectric state. Recently this criterion for ferroelectricity has been thoroughly investigated, particularly by William Cochran and Roger Cowley from the point of view of lattice dynamics. Most of the macroscopic theories are based on the assumption of a linear response of the substance to an electric field. Fröhlich mentioned that this need no longer hold after a catastrophe when $\omega_t \rightarrow 0$ and $\epsilon(0) \rightarrow \infty$ is reached, as is the case of ferroelectrics. If the response remains linear, transition to the metallic state is supposed to be most likely. The suggestion is made that such transitions should be studied in terms of ω_t and $\epsilon(0)$. In this connection Fröhlich forwarded a quite interesting general assumption, namely, that it is quite possible in some cases that transition from the nonmetallic to the metallic state might be preceded by a transition to a ferroelectric state.

Lattice dynamics has been considered for a certain number of years as a possible key to understanding ferroelectricity. A number of papers have been presented with this implicit assumption. At the symposium, Alexei A. Maradudin spoke on ferroelectricity and lattice anharmonicity.

An impressive set of recent experimental results on lattice dynamics of diatomic crystals of high dielectric constant such as PbS, PbTe and SnTe was presented by Cochran. There is no reason in principle why a diatomic crystal should not have a ferroelectric phase and Cochran undertook a check on the criterion for ferroelectricity stating that ω_t should vanish at the critical temperature for these materials. The dispersion curves for the directions of high symmetry are determined by standard neutron scattering techniques. In the three materials ω_t decreases fairly steeply as the wave vector decreases to zero, and for PbTe and SnTe in particular, the shape of the curve is very similar to that for $SrTiO_3$. For SnTe, ω_t is strongly temperature dependent. On the basis of the results presented, SnTe can be described as "paraelectric" with lattice dynamic properties similar to those of $SrTiO_3$. The system GeTe–SnTe has also been studied. It is supposed that the cubic structure of SnTe becomes stable at 0°K. The system GeTe–SnTe forms a complete solid solution with the transition temperature T_c falling smoothly as the tin content is increased. The transition in GeTe is a ferroelectric transition but the difference with the usual ferroelectrics may be that the direction of spontaneous polarization in GeTe cannot be controlled by an externally applied field. Structurally the transition in GeTe is one of the simplest ferroelectric transitions that could be devised.

A survey of the role of symmetry and symmetry changes of a crystal in phase transformation and ferroelectricity has been presented by Joseph L. Birman. In lattice theory of ferroelectricity an essential role is given to the anharmonic potential energy. Birman discussed the complete use of symmetry of the paraelectric and ferroelectric phases to construct from the normal modes lattice invariants (for the total lattice Hamiltonian) and covariants (for the electric-dipole-moment operator) such as anharmonic potential energy. Birman also reviewed attempts made to demonstrate the explicit role of the electronic states of a solid in the phase and symmetry changes leading to ferroelectricity. Attention was also drawn to the possibility of involving, in the interpretation of the phase changes that produce ferroelectricity, the distortions that occur in displacive ferroelectrics such as $BaTiO_3$, which are reminiscent of the mechanism of configurational instability of the Jahn-Teller effect. In the dynamic Jahn-Teller effect several molecular configurations resonate between several equivalent distorted configurations so that the search for the minimum-energy state requires the use of coupled electron-vibration eigenfunctions. Adjusting the configurational instability theorem, one can take as a general rule that essentially all degenerate electronic states in crystals are unstable by way of electron-phonon coupling. An interesting suggestion then is to elaborate a detailed microscopic mechanism using coupled electron and phonon eigenfunctions by which a displacive phase transition could be driven.

Surface and size effects on the stability of crystal lattices were discussed by Richard F. Wallis, first in the case of finite monatomic, linear, one-dimensional lattice with nearest- and next-nearest-neighbor interaction and also for the body-centered cubic lattice. Stability conditions were obtained for finite simple cubic and face-centered cubic lattices of various sizes and shapes. It was demonstrated that the criteria used for the stability based on the divergence of a particle mean-square displacement and that based on the discriminants of the force-constant matrix are equivalent. Both criteria essentially ensure that instability occurs when some squared normal-mode frequency goes through zero. This lattice-dynamical investigation on the stability of crystals was presented in the case of a simple model but was carried up to the point where explicit results are exhibited and can now be applied in more complicated and realistic models.

In a talk on the search for new ferroelectric materials Bernd T. Matthias, with his usual enthusiastic schematization, stated that, next to melting, ferroelectricity may be one of the most coöperative phenomena generally found in nature. Consequently, the number of ignored ferroelectrics is huge and the field of systematic investigations is largely open. It is believed that it should now be possible, simply by looking through the literature, to predict ferroelectricity or antiferroelectricity purely from nonferroelectric data. The periodicity of important discoveries in ferroelectrics as established by Matthias is by decades, but he admits that some tendency exists on speeding up at the present time. Matthias also brought out one of the most crucial and controversial aspects of ferroelectricity: the ferroelectric metal. He particularly insists that ferroelectricity and superconductivity seem to be entirely mutually exclusive. The mechanism by which superconductivity is prevented by ferroelectricity, or vice versa, is as yet unknown, but if ever eventually known, it is believed that it should illuminate the nature of both these coöperative phenomena quite thoroughly.

The number of materials in which ferroelectric behavior has been studied and the variety of phenomena observed was purposely limited in this symposium to give more emphasis on what is common and general in their behavior.

Special attention was devoted to KNO_3 because most of the essential work on the ferroelectric properties of this crystal has been done or initiated by the GM Research Laboratories. M. Nusimovici presented a detailed study of the lattice dynamics of KNO_3 in the three phases and some considerations, based on group theory, concerning the ferroelectric phase. Jack G. Gay has analyzed the structure and the stability of the ferroelectric phase of KNO_3 and James P. Nolta gave a detailed study of the ferroelectric properties of potassium nitrate in the form of polycrystalline thin films. Important size effects have been found.

In addition, the following were discussed: lithium niobate as a new type of ferroelectric (K. Nassau); light scattering (Herman Z. Cummins); infrared absorption (A. S. Barker); light modulation (Ivan P. Kaminow); film charging by ferroelectrics (Henry L. Stadler); ferroelectricity of ice (Lars Onsager).

Although no major new discoveries and completely elaborate theories were presented in this symposium, extremely stimulating discussions were engaged and, by its size and selection, it could be considered as one of the best examples of a successful symposium. Most of the participants left the General Motors Technical Center recharged with new ideas and stimulated for further research, which undoubtedly will lead to important results.

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3rd High-Energy Physics Conference in Canada

This conference, sponsored by the Canadian Association of Physicists to stimulate interest in high-energy physics in Canada, was held at McGill University on 5 Nov. 1966. There were about 75 participants, from Canada, the United States and elsewhere.

The conference was divided into three sections: high-energy experiments, high-energy theories and medium- to high-energy accelerators.

High-energy experiments. J. C. D. Prentice (Toronto) reported on a π^--p experiment at 3 GeV/c performed at the zero-gradient synchrotron. The process $\pi^- + p \rightarrow \pi^+ + N^{*-}(1236$ MeV) admits no single-particle exchange but may result by going through a direct-channel intermediate nucleon isobar state. The angular distribution for $N^{*-}(1236)$ measured in this experiment was consistent with $N^*(2650)$ as being the intermediate state. In the reaction $\pi^- + p \rightarrow \pi^- + \pi^+ + \pi^- + p$, ρ^0 and N^* were observed respectively from the π^--π^+ pair and the π^--p pair. These reactions $\pi^- + p \rightarrow \rho^0 + N^*$ were all peripherally produced except N^* (1688), for which the different angular distribution again suggested a direct-channel mechanism.

W. S. Chapman (Rutherford Laboratory and Atomic Energy of Canada Limited) described the production of nucleon isobars in p-p collisions between 2 and 8 GeV/c in an experiment done at the Rutherford Laboratory. In the latter experiment, nucleon isobars of masses 1236, 1410, 1519 and 1688 MeV were identified as peaks in the differential cross section $d^2\sigma/d\Omega dp$, where Ω and p are the solid angle and the momentum of the detected final-state proton. After subtracting background contributions, the isobar production cross section σ for each isobar was obtained as a func-