Ferroelectricity

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UNDER THE NAME OF FERROELECTRICS one classifies those materials which exhibit dielectric anomalies phenomenologically similar to the magnetic behavior of the ferromagnetics. Perhaps it would have been more logical to use the term Rochelle electrics, thus emphasizing the similarity in the dielectric behavior to that of Rochelle salt, for which this behavior was first discovered by J. Valasek (*1*).

In this discussion the known ferroelectrics will be listed, and the various theories that have been created to explain them will be examined.

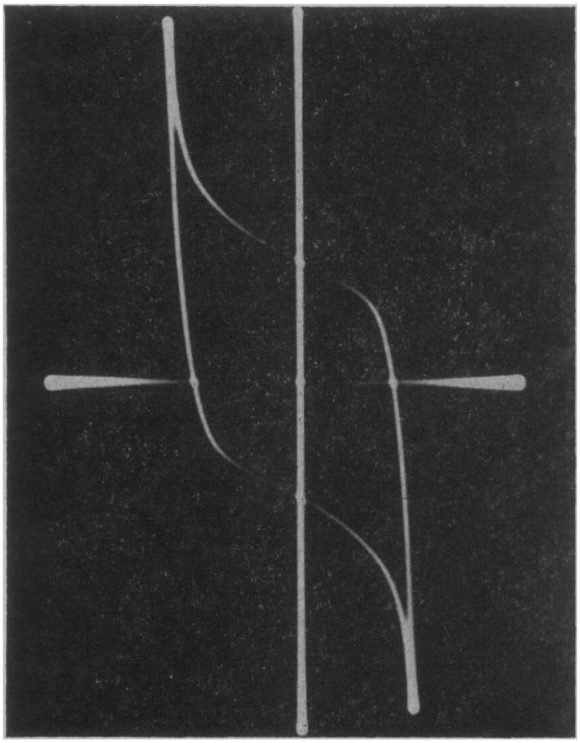

FIG. 1. Hysteresis between dielectric field and polarization.

Rochelle salt, the potassium sodium tartrate, was the first crystal to be shown to haxe extremely high dielectric constants—of the order of 10^3. This, however, is confined to the temperature interval between $-18°$ C and $+24°$ C and to one crystallographic direction, parallel to the a-axis. In analogy to ferromagnetism, the two temperatures above and below which the ferroelectric behavior disappears are called the two Curie points of Rochelle salt. Simultaneously with the change in the dielectric constant, the piezoelectric constant d_{14} goes through very high values. In the ferroelectric range a hysteresis loop between electric field and polarization is observed, indicating the existence of a spontaneous polarization. Outside the ferroelectric range the dielectric constant decreases and the spontaneous polarization disappears. (Figs. 1, 2.)

Until now none of the crystals isomorphous with Rochelle salt had shown any similar dielectric anomalies. The only changes which did not drastically alter the ferroelectric activity of Rochelle salt were a partial substitution of hydrogen by deuterium, and hydrostatic pressure. These result in a spreading of the ferroelectric range. Otherwise hardly anything else could be done to the salt which would not destroy the ferroelectric properties. If only a small percentage of potassium is replaced by rubidium, ammonium, or thallium, for example, the dielectric anomalies disappear entirely.

Only recently (*2*) it was noticed that Scholz's (*3*) measurements on $LiNH_4C_4H_4O_6 \cdot H_2O$ at temperatures above 125° K show a steep rise in certain piezoelectric moduli for this crystal with decreasing temperature, a reasonable extrapolation indicating that the piezo-moduli become infinitely large in the neighborhood of 100° K. This behavior leads us to expect the occurrence of ferroelectricity in lithium ammonium tartrate at low temperatures, a hypothesis that has now been confirmed by experiment (*2*).

Fig. 3 shows the temperature variation of ε_b, the plate with the electric field parallel to the b-axis of the crystal. The sharp peak at 98.5° K marks an upper Curie point, below which the crystal becomes ferroelectric. Polarization versus electric field exhibits the well-known hysteresis loop, though the average value

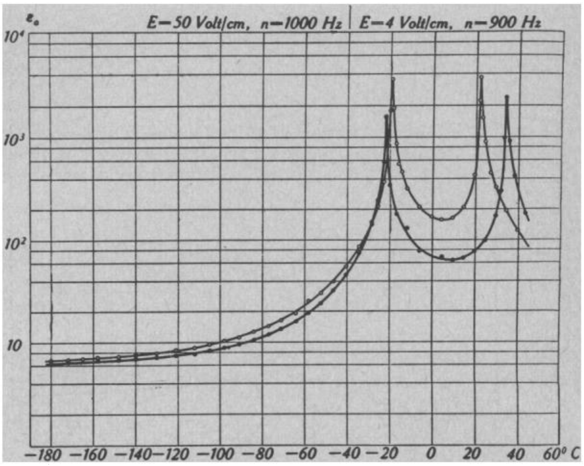

FIG. 2. Dielectric constant of Rochelle salt (*17*).

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[1] On leave of absence at the University of Chicago.

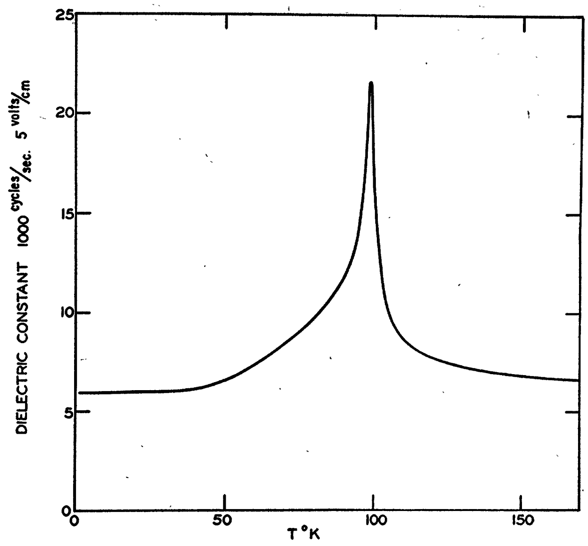


FIG. 3. Temperature variation of dielectric constant Li $NH_4C_4H_4O_6 \cdot H_2O$.

of the dielectric constant is low compared to average values for other ferroelectric crystals, including Rochelle salt. The absence of a lower Curie point may be inferred from the monotonic variation of ε_b from the upper Curie point down to 1.3° K, the lowest temperature of measurement.

The above discovery immediately raised the question as to whether a similar type of ferroelectric behavior might occur in other isomorphous crystals, or whether lithium ammonium tartrate would turn out to be another singular case like Rochelle salt. Although the only other isomorphous crystal studied by Scholz (*3*), $LiKC_4H_4O_6 \cdot H_2O$, gave no marked variation of piezo-moduli with temperature, this did not seem unreasonable in view of the difference between the K^+ and NH_4^+ ions. It is obvious that ferroelectricity will be *less* disturbed in the replacement of NH_4^+ by the more nearly isosteric Rb^+ or Tl^+ ions.

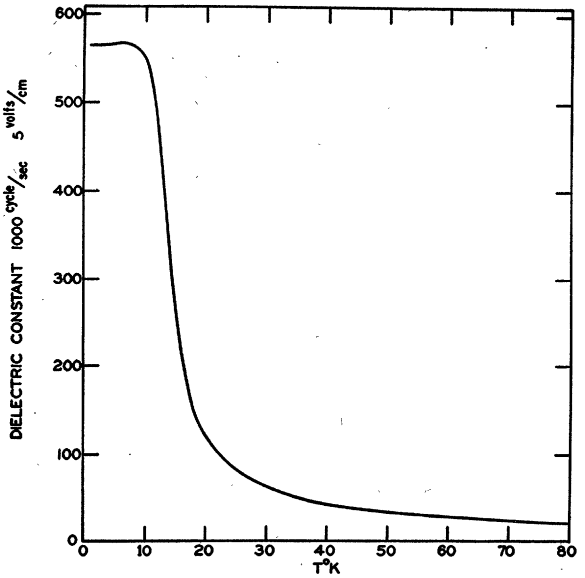


FIG. 4. Temperature variation of dielectric constant Li $TlC_4H_4O_6 \cdot H_2O$.

Fig. 4 shows the temperature variation of the dielectric constant, ε_a, of a crystal of $LiTlC_4H_4O_6 \cdot H_2O$ with the electric field applied parallel to the *a*-axis. With decreasing temperature ε_a showed an unusually rapid rise between liquid hydrogen and liquid helium temperatures, but for a given field strength eventually passed through a very flat maximum and tended to a steady value as absolute zero was approached. At liquid helium temperature, however, ε_a was extremely sensitive to small changes in field strength owing to the fact that *below* 10 (±1)° K the crystal exhibited, as expected, a ferroelectric hysteresis loop.

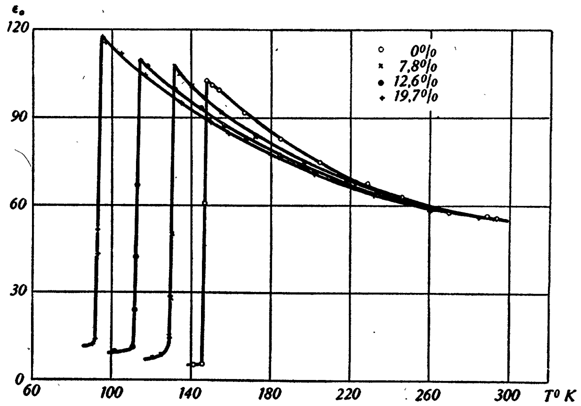


FIG. 5. Shift of the transition point of $(NH_4, Tl)\ H_2PO_4$ with varying Tl-content (*5*).

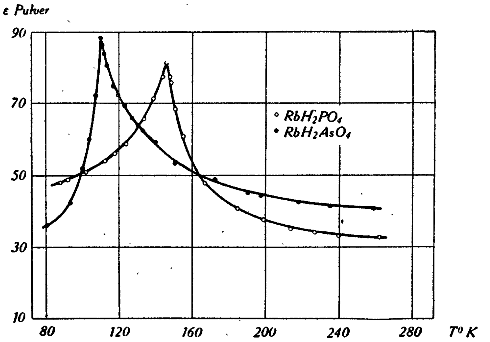


FIG. 6. Dielectric constant RbH_2PO_4 and RbH_2AsO_4 powder (*6*).

In 1935 two other ferroelectric crystals were discovered by Busch and Scherrer (*4*). They were the tetragonal potassium dihydrogen phosphate and the corresponding arsenate, KH_2PO_4 and KH_2AsO_4. Only one Curie point was observed, the temperature below which the crystals became and remained ferroelectric. In the case of the corresponding ammonium salts, as the temperature is lowered an ammonium transition intervenes and a ferroelectric condition does not occur

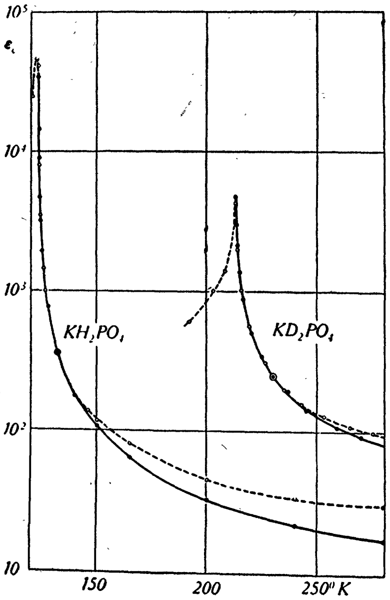


FIG. 7. Dielectric constant of normal and heavy potassium phosphate (*21*).

(*5*). The ammonium transition is due to the quadrupole moment interaction of the NH_4 groups.

Their ordered arrangement below the transition temperature modifies the internal field to an extent which prevents the final occurrence of ferroelectricity. Screening the NH_4 ions by spherical symmetric thallium ions weakens the interaction and therefore lowers the transition temperature (Fig. 5). But it was possible to show later that all other crystals, isomorphous to the K-salt at room temperatures, such as the rubidium salts (*6*), do also become ferroelectric. If hydrogen is replaced by deuterium in KH_2PO_4 the Curie point is shifted to considerably higher temperatures (Figs. *6, 7*).

The next ferroelectric crystal to be discovered was $BaTiO_3$. This was found more or less simultaneously in the United States, England, and Russia, after titanate ceramics with high dielectric constants had been investigated for the preceding 15 years. Single crystals of the compound were first grown in Zurich (*7*). Again there was only one Curie point, and it could be shifted to higher or lower temperatures by partially replacing the Ba ions with lead or strontium. However, it was then not possible to detect ferroelectricity in any other of the isomorphous titanates. In these earlier stages of investigation it was therefore not yet quite clear whether barium titanate was again an isolated case like Rochelle salt.

In 1949, in following up a hypothesis which will be discussed in detail later, several new ferroelectric crystals isomorphous to barium titanate were discovered, in the alkali niobates and tantalates (*8*). As the assumptions made were almost independent of the crystal structure, two new ferroelectric crystal classes were found subsequently in the ilmenite (*9*) and the ReO_3 (*10*) structures. The crystals in the first system were lithium niobate and tantalate, and in the latter tungsten trioxide.

Theoretical aspects: Rochelle salt. Many theories have been advanced in attempts to account for the ferroelectricity of Rochelle salt, the phosphates, and barium titanate. In addition, several review articles have recently appeared which deal with these materials (*11, 12*).

Rochelle salt, though the first to be discovered (some 70 years ago), is still the hardest to explain. Early theories about rotating dipoles have long been forgotten. Today a possible way seems to be Ubbelhode's application (*13*) of Huggins treatment of the free hydrogen bond (*14*). This bond presumably changes from a one- to a two-well potential if the bond length exceeds 2.59 A. This is just about the length of the hydrogen bond in Rochelle salt (*15*). This fact can explain only the lower Curie point, however. Even from a phenomenological point of view it is difficult to account for the *two* Curie points.

Mueller's interaction theory (*16*), however, should be mentioned with respect to a phenomenological explanation of both Curie points. He arrives at the conclusion that *two* Curie points occur as a result of the electromechanical interaction. If the corresponding properties of a completely clamped crystal could be measured, then the dielectric susceptibility should show *one* maximum only near 5° C. No experimental verification could as yet be obtained.

The small change in ferroelectric properties with the replacement of hydrogen by deuterium (*17*) certainly does not stress the importance of the hydrogen bond. It looks much more as if Rochelle salt is merely an accident of nature which happens to fall upon a stoichiometrically well-defined compound. Sufficiently outside the small range of temperature or crystallographic dimensions no anomalies can be observed.

In comparing the recently discovered ferroelectric tartrates with Rochelle salt, it has to be borne in mind that, although the crystal symmetry is the same in each case, the axial ratios are quite different, and in addition Rochelle salt has *four* molecules of water of crystallization compared to *one* molecule in both of the new crystals. In view of this fact, it is somewhat surprising that practically the same value of spontaneous polarization is observed for each crystal, which may indicate again that the water molecules play a relatively unimportant role in the ferroelectric behavior. The low value of the dielectric constant and unusual (*b*) direction of ferroelectric behavior in lithium ammonium tartrate are possibly the result of an interaction between ammonium ions of the type observed in $NH_4H_2PO_4$ (*5*). The new results strengthen the assumption that the lower Curie point in Rochelle salt is somewhat accidental. A comparison of the lithium thallium tartrate data with those for potassium tantalate (*8*) seems to indicate that sharp dielectric constant peaks do not occur near absolute zero, presumably because of an increase of time of alignment.

The dihydrogen phosphates. The tetragonal dihydrogen phosphates and arsenates have permitted more insight. Comparison of the isomorphous crystals shows the tetragonal H_2PO_4 lattice to be ferroelectric in general. The PO_4 tetrahedra are linked one to another by hydrogen bonds. The statistical theory of the position of these hydrogens was carried out by Slater (*19*) in a well-known paper. As the hydrogen bond is nearly perpendicular to the direction of the spontaneous polarization parallel to the *c*-axis (*20*), this polarization seems to be created rather by the induced moment in the PO_4 groups than by the moment of the hydrogen bond itself. Replacing the hydrogen by deuterium, the Curie point of KH_2PO_4 is shifted to higher temperatures (*21*). This is excellent confirmation of the essential role of the hydrogen bond as the cause of ferroelectricity in this case. The zero point energy of the deuterium is about 1.4 times smaller than that of the hydrogen, and a larger thermal energy is therefore required to destroy the ordered state (*22*).

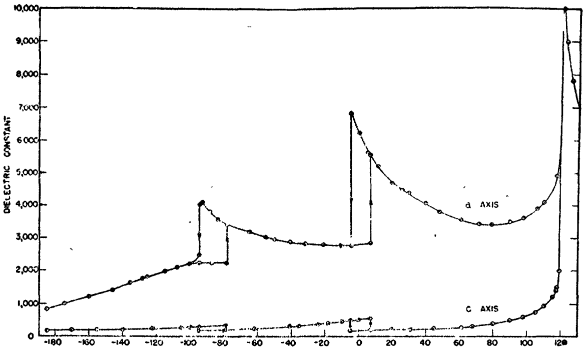


FIG. 8. Dielectric constant of barium titanate (Merz, W. *Phys. Rev.*, **76**, 1221 [1949]).

Order-disorder and displacive transitions. This brings us to the differences in ferroelectric transitions first pointed out by Tisza (*23*). In Rochelle salt outside the ferroelectric region there seems to be no ordered state, at either high or low temperatures, which has to be overcome by the thermal motion. We have here a displacive transformation, whereas the transition in KH_2PO_4 is an order-disorder phenomenon.

According to Tisza, no dipoles are present in Rochelle salt outside its ferroelectric region, whereas they continue to exist in KH_2PO_4 above the Curie point in a disordered arrangement. This point of view has been strengthened by the small anomalies of the specific heat in the case of displacive transformations.

For barium titanate the small anomaly of the specific heat at the Curie point again indicated clearly a displacive transformation like the one in Rochelle salt. The atomic mechanism is, however, quite different. TiO_2 and several metatitanates all have very high dielectric constants, ranging up to 400. The same mechanism in barium titanate causes a dielectric constant which is so large as to produce a spontaneous polarization below a certain critical temperature, the Curie point (Figs. *8*, *9*).

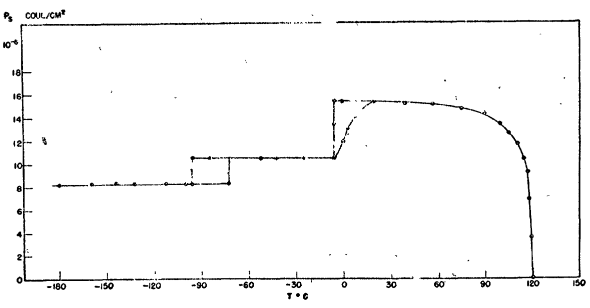


FIG. 9. Spontaneous polarization of a $BaTiO_3$ single domain crystal (Merz, W. *Phys. Rev.*, **76**, 459 [1949]).

In the case of barium titanate, fortunately, the structure is well known, and no ambiguities exist such as the positions of hydrogens. The crystal structure is that of perovskite, the unit cell of which is a cube in the idealized case (Fig. 10). The Ba-ions occupy cube corners, the oxygens face centers, and the titanium is in the cube center. One of the first explanations was the "rattling" theory, which originated in England and which assumed the motion of the titanium ion within a too large oxygen octahedron (*24*). The order of magnitude for the amplitude of the titanium can be evaluated from the saturation polarization. Considerations of the ionic radii, as well as x-ray investigation, finally spoke against this assumption.

A different approach was that of Jonkers and van Santen (*25*). According to these investigators, $BaTiO_3$ is one of the few cases in which the polarizability per unit volume increases to the limit where a spontaneous polarization will occur. This is easily seen in Clausius-Mosotti's formula for the dielectric constant:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} N\Sigma\alpha_{EL} + \alpha_{ion} + \frac{\mu^2}{3KT} \qquad (1)$$

The summation extends over ionic as well as electronic polarizabilities of the simple oxides which are the constituents of the whole compound. $BaO + TiO_2$ now give a value which brings the right-hand side of equation (1) close to unity, thus giving an infinite dielectric constant. Doubts have been raised as to the validity of this partial summation, which in itself, furthermore, only reduces the problem of double oxides to that of the single one. These theories, as well as the ones to be mentioned later (*26*), confirm barium titanate as a ferroelectric, but do not permit any predictions concerning the occurrence of ferroelectricity in other compounds or systems. A different approach was therefore tried at Bell Telephone Laboratories.

Prediction of new displacive ferroelectrics: perovskites. The dielectric constant of TiO_2, *as well as* those of all pseudo-cubic (perovskite) metatitanates, was unusually high. One had therefore to assume that it was primarily the Ti-O (titanium surrounded by 6 oxygens in form of an octahedron) octahedra which contributed to the high dielectric constant, and by some coincidence caused ferroelectricity in barium

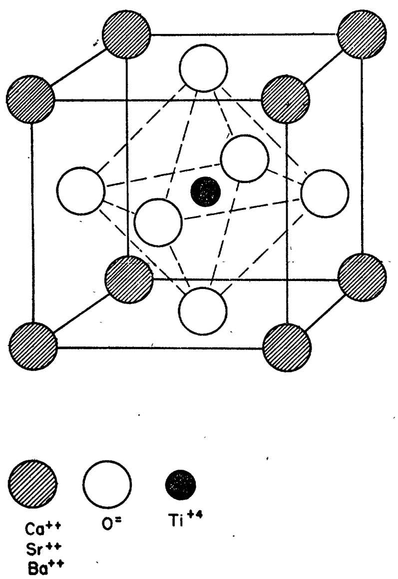


FIG. 10. Unit cell of the idealized perovskite structure.

titanate. The problem was therefore once again to account for the high dielectric constant of rutile, a matter that had already been attacked by Eucken and Beuchner as early as 1934 (*27*). As later shown by Slater (*26*) and by Jaynes and Wigner (*28*), it seemed reasonable to consider the octahedron as a *whole,* the high polarizability of oxygen being essential. It should therefore be possible to obtain the same high polarizabilities in other similar oxygen octahedra that had a central atom other than titanium; yet the corresponding stannates and zirconates gave comparatively low dielectric constants. Sn^{+4} did not have a noble gas configuration, however, and Zr^{+4} was much larger than Ti^{+4}. This viewpoint has been strengthened in two recent papers from Japan. Starting from the hypothesis for the critical size of the Ti-O octahedron, Nomura and Sawada (*29*) have repeated a coincidence similar to barium titanate by forming solid solutions of strontium and lead titanate which again were ferroelectric. On the other hand, reports on an anomaly of the dielectric constant in $PbZrO_3$ indicate quite a different behavior (*30*). No spontaneous polarization can be detected, and the large anomaly of the specific heat points to an order-disorder transformation. In order to obtain oxygen octahedra in which the oxygen to central atom distance was close to that in the $Ti\text{-}O_6$ octahedron, and in which the electron configuration of the central ion was that of a noble gas, one had to turn to the metaniobates and tantalates. They indeed proved to be ferroelectric (*8*) (Fig. 11). Since niobium and tantalum in the noble gas configuration are pentavalent, the valency of the big cation had to be reduced by one in order to restore electric neutrality. This leads to the alkali metaniobates and tantalates $KNbO_3$, $NaNbO_3$, $KTaO_3$ and $NaTaO_3$, all of which proved to be ferroelectric with Curie points between 13° K and 800° K (*18*).

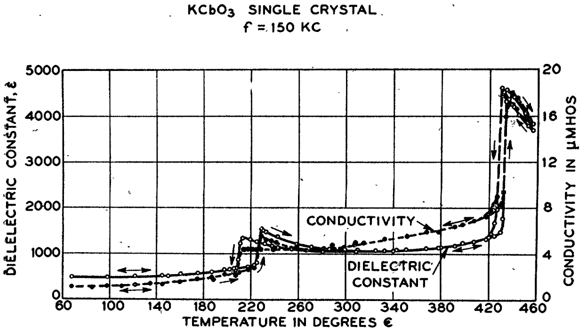
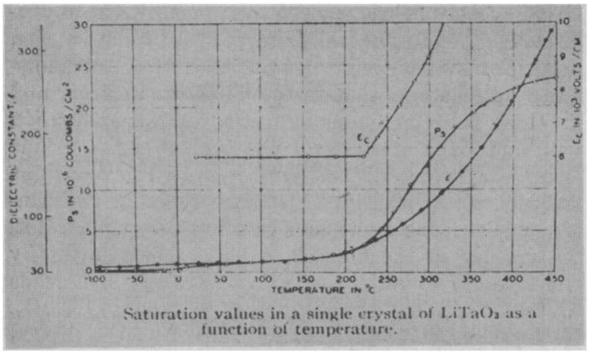


FIG. 11. Dielectric constant of a $KCbO_3$ crystal.

One step further in the direction of similar octahedra leads to tungsten trioxide (*10*), which again proved to be ferroelectric. Although the above-mentioned compounds are still isomorphous with barium titanate, WO_3 crystallizes in a somewhat different crystal structure, which is a pseudo-morph of ReO_3. This is a perovskite system in which the cube corners of the unit cell are omitted.

Ferroelectrics in the ilmenite system. It was important to realize that the hypothesis of the oxygen octrahedra of critical size and electron configuration worked as well even in different crystal classes. Therefore compounds in the ilmenite system were considered next. So far, most theories, in order to prove their respective statements, made use of the fact that dielectric constants of double oxides, crystallizing in the rhombohedral ilmenite system, were very low compared to those in the perovskite system (*12, 25, 26*). These assumptions are quite erroneous, however. Single crystals of the hexagonal barium titanate already had shown dielectric constants up to 200 (*31*). In the perovskite system it had become obvious that the $Ti\text{-}O_6$ octahedra were less favorable for creation of ferroelectricity than the niobium or tantalum octahedra. We therefore began an investigation of corresponding compounds of the ilmenite system: $LiNbO_3$ and $LiTaO_3$. The dielectric constants measured in the beginning were quite low, between 15 and 30—that is, of the same order of magnitude as those reported for the other double oxides in the ilmenite system, measured on ceramics. Upon increasing the electric field strength it immediately became apparent that these crystals were very strongly polarized, and only the extremely high coercive field prevented the detection by bridge measurements (*9*). The hysteresis loop at 200° C—e.g., the dependence of the dielectric polarization upon the electric field—was a perfect rectangle. The value of the saturation polarization of $25 \cdot 10^{-6}$ Clb/cm^2 so measured was nearly twice that of the crystals in the perovskite system (Fig. 12). Ceramic samples of these compounds gave hardly any effect at all, however. This is understandable, considering the much lower symmetry of the ilmenite system as compared to the perovskite structure. It would therefore be necessary to investigate single crystals of the



Saturation values in a single crystal of $LiTaO_3$ as a function of temperature.

FIG. 12. Dielectric behavior of a $LiTaO_3$ crystal.

rhombohedral metatitanates before any conclusions as to their dielectric behavior could be reached.

We have tried to show that all metal-oxygen octahedra which fulfill certain conditions will always cause very high polarizabilities and are therefore the cause of ferroelectricity in those compounds that do not contain hydrogen. Other octahedra which do not satisfy the conditions may give rise to many different kinds of transitions, but never give high dielectric constants or ferroelectricity (*32*). The theoretical aspects concerning these octahedra have been and will be published by Jaynes and Wigner (*28*). The recent paper by Slater (*26*) on the correction of the Lorentz factor in barium titanate confines itself to this compound. Slater comes to the conclusion that the TiO strings running through the lattice are the essential factor for the occurrence of ferroelectricity.

Lower Curie point in $LiTaO_3$. Except for Rochelle salt, there never had been observed a lower Curie point—that is, a temperature *below* which the spontaneous polarization disappears completely. Only recently in $LiTaO_3$ a sharp decrease of the spontaneous polarization with decreasing temperature has been measured (*9*). A numerical treatment will be able to decide whether this is due to the stronger interaction between neighboring octahedra on account of their closer contact with each other. In the ilmenite structure neighboring octahedra share corners *and* edges, whereas in the perovskite system the octahedra only share corners.

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Technical Papers

The Mucopolysaccharides of the Ground Substance of Connective Tissue[1]

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The dramatic effects of cortisone and adrenocorticotrophic hormone (ACTH) on the manifestations of rheumatic diseases, as well as on some not classified as rheumatic, have forcefully reemphasized the importance of the connective tissues in the mechanism of a variety of disorders. It seems remarkable that we still know so little about the biochemistry and physiology of the mesenchyma, even though its contribution to biological processes and its paramount importance in pathology had been recognized long before the advent of cortisone.

In the past 20 years, the ground substance(s) of the mesenchyma have been studied extensively. The reawakened interest in these tissues was due in part to the isolation and characterization of some of the

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