Neutron Diffraction Studies of Ferroelectrics*

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Neutrons have been used to somewhat greater advantage than X-rays in determining ferroelectric structures. This has been mostly because so many ferroelectrics contain light atoms in the presence of relatively heavy ones. Two of the most important ferroelectrics, BaTiO₃ and Rochelle salt, are discussed as examples. In both cases it seems that X-ray solutions are not feasible. It has been possible to obtain a neutron solution for the BaTiO₃ structure, but because of the pseudosymmetric nature of the structure this turned out to be a surprisingly difficult problem. The outlook for a detailed solution of the ferroelectric structure of Rochelle salt is not very hopeful; however, some useful results have been obtained. An interesting by-product of the neutron study of this crystal has been the discovery that irradiation by X-rays and γ -rays produces serious microstructural changes. Previously the effects of radiation on Rochelle salt had been ascribed entirely to macroscopic changes.

A ferroelectric crystal structure always belongs to one of the pyroelectric classes of symmetry, and, as is well known, the polarity of the structure can be reversed by applying an external field. As may be inferred from this reversibility, the structure deviates only slightly from non-pyroelectric symmetry, and in fact it transforms to this at the Curie point. As small as the deviations may be, it is from these deviations, and from them alone, that spontaneous polarization arises. Precise structural information is therefore of fundamental importance to an understanding of the ferroelectric properties of a crystal.

Neutrons have been used to somewhat greater advantage than X-rays for structural studies of ferroelectrics. The main reason for this is that so many ferroelectrics contain light atoms in the presence of relatively heavy ones, and neutrons are especially useful for this sort of problem. The most striking examples are provided by the hydrogen-bonded ferroelectrics. Neutrons also enjoy some advantages which result from angular independence of the scattering lengths. At high $\sin \theta / \lambda$, where the data are most sensitive to small displacements from higher symmetry positions, one may encounter a substantial degree of uncertainty in the X-ray scattering factors. Although usually of less importance, there are also uncertainties which may exist at low angles

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due to lack of knowledge of effective atomic ionization states. In addition, again because of the constant scattering lengths, it is possible to achieve greater resolution and acuracy with neutron data. Finally, it appears that the irradiation dosage a ferroelectric crystal receives during the collection of X-ray data may be sufficient, in some cases at least, to cause enough microstructural change to cast some doubt on the validity of X-ray results. This point was raised some time ago by Chynoweth¹⁾, but it is only recently that we have had substantial evidence that this could be the case.

In making these remarks I do not wish to minimize the importance of X-ray work. Every neutron problem really begins as an X-ray problem. One can work much more rapidly with X-rays in collecting data. It is usually much easier to determine space groups with X-rays than with neutrons. Lattice constants can be determined with much higher precision with X-rays. There are also cases where X-rays are more sensitive to certain atomic positions. The techniques of anomalous dispersion, with which the orientation of the structure may be checked to compare with the direction of spontaneous polarization, are much more widely applicable with X-rays. Thus, while neutrons have been used to greater advantage, in the sense that they usually yield more complete and more reliable structures, it is most sensible to regard X-ray and neutron diffraction as

complementary tools.

A number of X-ray and neutron diffraction studies of ferroelectric structures have been published in recent years, and it might appear that the elucidation of the structural nature of ferroelectricity is a matter of routine application of standard crystallographic methods. One of the purposes of this paper is to demonstrate the inaccuracy of such a view. The pseudosymmetric character of ferroelectric structures introduces some difficulties not ordinarily encountered in most structure analyses. These will become apparent in the discussion of the two examples chosen to illustrate the use of neutron diffraction in the study of ferroelectric structures. I have chosen probably the simplest and the most complex structures among the ferroelectrics. They are also probably the most important ones: BaTiO₃ and Rochelle salt.

First we might give some brief attention to the background of these crystals as structure problems, and to the advantages of neutrons in their particular cases. This discussion could be made very brief indeed by simply saying that it now seems certain that in neither case is a detailed X-ray solution possible, and hence any additional information that may be obtained with neutrons is information gained. It will perhaps be instructive to say more than this, however. Clearly there are advantages for neutrons in the case of Rochelle salt. Almost half of the atoms are hydrogens, and since the first X-ray analysis of Beevers and Hughes²⁾ there has been reason to believe that it is with these atoms that the key to the ferroelectric behavior would be found. More important than this, however, is our recent demonstration that the ferroelectric structure of Rochelle salt is seriously affected by ionizing radiation. Thus, it seems that if a meaningful solution of this structure is to be obtained at all, it can only be done with neutrons. If this might be considered some sort of triumph for neutrons, it is a hollow one indeed. The problem is now far more formidable than it would otherwise have been. We had hoped that the low X-ray scattering of hydrogen might be turned to advantage by permitting us to divide this complex problem into two independent parts. To this end, cooperative X-ray studies were

undertaken at Penn State, culminating in the full 3-dimensional study which only recently was completed by Krstanovic, Okaya, and Pepinsky³⁾. Their efforts have by no means been a total loss, since their work provides the best imformation available on the 3-dimensional structure (the neutron work has thus far been confined to two dimensions). Nevertheless, it now seems clear that there is little hope for the original purpose of eliminating the non-hydrogen atoms from the neutron refinement.

The background to the BaTiO₃ problem is somewhat different. At one time it appeared that a complete X-ray determination of the ferroelectric tetragonal phase had been accomplished. I believe that when Evans⁴⁾ published a preliminary note on this work. he had obtained the lowest R factor (4.7%)that had ever been reached in a structure analysis. This work was done with only a single isotropic crystal temperature parameter, and Evans decided to check his results by general least squares calculations with anisotropic atomic temperature parameters. He discovered that despite the high accuracy of his data, and despite an even lower Rfactor (3.7%), the problem was essentially indeterminate. For a long time these results were available only in report form⁵⁾, but recently they have been submitted for publication⁶⁾. The reasons for indeterminacy have been analysed in detail by Geller⁷⁾.

Following a suggestion of Evans that the structure might be soluble with neutrons, we made some preliminary calculations which showed quite clearly that neutrons are far more sensitive than X-rays to the ferroelectric displacements. The principal reason for this is that the neutron scattering length magnitudes do not differ greatly for the various atoms, whereas with X-rays the diffracted intensities are dominated by the heavy Ba scattering. The relative sensitivity may be illustrated by comparing reflection pairs of the type (h0l) and (l0h). These are equivalent when the crystal is cubic. The largest differences in such pairs for both X-rays and neutrons occur for h odd l even. If we consider structure factors for the (104) and (401) pair, for example, we find a difference of about 3% for X-rays, but over 70% for neutrons. Higher angle pairs are even more

favorable for neutrons.

So much for these preliminary remarks, and let us go on to see what can be made of the advantages of neutrons for these structures. We shall begin with BaTiO₃. Above its Curie point this crystal has the cubic perovskite structure with Ba on the cell corners, Ti at the body center, and the O's on the face centers. Below the Curie point the structure becomes tetragonal with spontaneous polarization developing parallel to the *c*-axis. There are transformations to other ferroelectric phases below room temperature, but we shall not be concerned with them here. In the tetragonal phase, all of the atoms are free from symmetry restrictions on their z coordinates, although we must fix one atom so as to define the cell origin. Since Ba is usually placed at the cubic cell origin, it is a convenient choice for locating the tetragonal origin. The three oxygens are no longer equivalent, but instead are of two types: O_I, slightly displaced in z from $(\frac{1}{2}\frac{1}{2}0)$; and O_{II}, slightly displaced in z from $(\frac{1}{2}0\frac{1}{2})$ and $(0\frac{1}{2}\frac{1}{2})$. There are three anisotropic temperature parameters for O_{II} and two for each of the other atoms. Hence, there are thirteen parameters: three z coordinates, nine temperature parameters, and a scale factor.

The first neutron refinement was done using 50 (h0l) reflections with isotropic atomic temperature parameters, and gave a very low R factor (3.0%). Like Evans, we were confident that the model would check out in a more complete analysis, and quickly published a note on our results⁸⁾. We too were later to find ourselves in trouble when a general refinement was attempted. The only difference in our story is that there is a happy ending. Since for a time the issue was in doubt, however, it may seem strange that we did not profit more fully from Evans' experience. The reason is that tests were made which indicated that there were no difficulties with the parameter interactions Evans considered to be the ones that led to indeterminacy. It is now known from Geller's work that these interactions are not the only serious ones. We also know now that while our early conclusions were correct on the Evans interactions, a serious interaction does occur in the neutron case between z_{Ti} and

the B_{33} temperature parameter for Ba. The latter is associated the thermal vibrations of Ba in the *c* direction. We shall limit our discussion largely to these two parameters.

The coupling between z_{T1} and $B_{33}(Ba)$ first showed in general least squares calculations using 69 reflections. In this and subsequent refinement series the program of Busing and Levy⁹⁾ was used. $B_{33}(Ba)$ behaved erratically from cycle to cycle and had unusually large standard deviations. Also, the magnitude was larger than any other temperature parameter in the structure, which seemed unreasonable because of the heaviness of the Ba atom. While z_{Ti} did not take on obviously unreasonable values, it did show noticeably large standard deviations when compared with the z's for the oxygens. Also, the parameter oscillated somewhat from cycle to cycle, with the mean value being significantly larger than that of our original model; about 0.023 as compared to the old 0.014.

With clear evidence for a disturbing degree of parameter interaction, we investigated this further by making several types of calculations. In the first of these, the possibility of an obscured $B_{33}(Ba)$ and z_{Ba} interaction was investigated, and rejected, by locating the origin relative to O_{II}. In the second type, B_{33} (Ba) was held constant over a range of values which we knew must include the proper one. This disclosed an almost linear dependence between z_{Ti} and B_{33} (Ba). Next we made a more general investigation by extracting the correlation matrix, and as expected the $B_{33}(Ba)$ - z_{Ti} coefficient was very close to one: 0.98. These calculations also disclosed some appreciable degree of coupling in three other cases, but none of these were seriously affecting the determination of z displacements. Finally, we began to investigate the effects of including (*hhl*) type reflections in the calculations. A small number had been included before, but now these were increased to give a total of 84 (h0l) and (hhl) reflections. Refinement calculations now converged smoothly, and it was evident that the interaction problem had been overcome. The standard deviations for z_{Ti} and $B_{33}(Ba)$ were still a little high relative to the other parameters, showing some residual coupling, but refinement was not being hindered.

This is the happy ending in so far as the

parameter interactions are concerned, but it is not quite the end of the structure determination. The final value of $B_{33}(Ba)$ turned out to be 0.66Å², which is still higher than any of the other temperature parameters. A value of about 0.3 is what was expected. This would agree well with what Evans found by X-rays, and despite his other difficulties, he should have obtained reasonably good Ba temperature parameters. Hence, we are now investigating the possibility of systematic errors in the data. Double-Bragg scattering has been rejected as a serious source of error because a considerable fraction of the data was taken at three different wavelengths, and almost every reflection was observed at two wavelengths. The wavelength studies have also given assurance that the data can not be greatly affected by extinction. Obvious cases were omitted in the refinement. In contrast to double-Bragg scattering, the effects of extinction are unidirectional, however, so that even for small corrections, the collective effect may be significant. This we are studying now. The only thing that can be reported at this time is that arbitrary corrections for a few of the strongest reflections did result in a significant drop in B_{33} (Ba) with very little change in the other parameters. The next step will be to correct the data systematically with the computing program of Hamilton.¹⁰⁾

Now let us spend the remaining minutes on Rochelle salt. There are 504 parameters to be determined in a 3-dimensional analysis of this structure, and even in the 2-dimensional projection with which we have been working, there are 280. In comparison to BaTiO₃ this is indeed a staggering problem. With the difficulties encountered with BaTiO₃ what hope can there be for a detailed solution for Rochelle salt? I am afraid that I cannot give a very optimistic answer. There is perhaps a glimmer of hope if several thousand very accurate neutron data are collected for a 3-dimensional attack on the structure, but even if a solution is feasible, the least squares computing problem becomes practically unmanageable. The refinement could perhaps be handled by Fourier difference methods.

If the prospects for a detailed analysis are so bleak, have there been any worth

while returns in the neutron studies? Here an affirmative answer can be given. Before going into this, however, some remarks might be made on why we once had an optimistic view of the problem, and on what happened in the attempted analysis that led us to change this view. The principal reason for optimism has already been indicated. We had thought that X-rays could be used to fix the positions of the non-hydrogen atoms. Also, to strengthen further the attack on the problem, data were collected from both deuterated and hydrogenous crystals. In addition, it is only recently that the seriousness of pseudo-symmetric parameter interactions has been fully appreciated, and the complexity of the problem was being greatly underestimated.

In the non-ferroelectric orthorhombic phases the space group is $P2_12_12_1$, and there are four symmetry-related NaKC4H4O6·4H2O formula units in the unit cell. The 21 axis parallel to b is destroyed in the transition to the ferroelectric phase, and the symmetry becomes monoclinic $P2_1$. There are now 56 symmetryunrelated atoms whose positions must be determined. These can be considered in pairs, which we might call pseudo-symmetric mates, that in the orthorhombic cell were related by the 2_1 axis. From the experience of BaTiO₃ a great variety of parameter interactions can be expected in this structure, but certainly the parameters of the pseudosymmetric mates will be involved in the most serious of these.

The first step in the neutron analysis was that of establishing approximate hydrogen positions. We began by assuming a model based on the Beevers and Hughes structure. Most of their hydrogen bond network was found to be correct but there were some differences which we shall come back to later. Next some preliminary refinement attempts were made with Fourier difference maps. The X-ray work at Penn State was proceeding in parallel with the neutron study. While the general agreement between the two analyses did not seem to be too bad, some inconsistencies began to develop. At first it was thought that these would be resolved, and that the X-ray results could be used to reduce the neutron problem to one of hydrogen positions. Despite many calculations

we never felt sufficient confidence in the Xray results to do this. A principal point of disagreement involved the odd (0k0) reflections. These reflections are the only new reflections that become possible in the transition from $P2_12_12$ to $P2_1$. While rather weak, they are clearly visible with neutrons, but have never been detected in an X-ray study. For this reason Beevers and Hughes assumed that the only ferroelectric displacements were those of hydrogens. While some of the early neutron work seemed to agree with this assumption¹¹⁾, we were able to disprove it later by comparing sets of odd (0k0)'s collected from deuterated and hydrogenous crystals. If only hydrogens became displaced, then these two sets should differ only by a simple scale factor. This was far from being the case, and hence other atoms had to be involved.

Several neutron and X-ray calculations were tried but essentially an impasse had been reached and eventually the problem was laid aside. It was picked up again when Vand and Pepinsky¹²⁾ developed a computing program (a modification of Sayre's program)¹³⁾ capable of handling the least squares refinements with isotropic temperature parameters. Our intention was to get the best isotropic approximation to a solution for both neutron data sets and the X-ray data, compare the three refinements for consistency, and then to take care of any thermal anisotropy by going back to Fourier difference methods. At one point this approach seemed to be working very well, but on careful analysis of what were to have been the final calculations before fixing the non-hydrogen positions, the true magnitude of the problem began to emerge. The persisting inconsistencies with X-rays were one matter, but it was becoming clear that the basic difficulty was intrinsic to the pseudo-symmetric character of the structure. This could not be investigated properly without general least squares analysis, and a suitable program did not exist. The problem was again laid aside until two developments caused renewed interest:

(1) The Busing and Levy program became available.

(2) We began to suspect that X-rays might be causing microstructural changes in the ferroelectric phase of Rochelle salt, and managed to prove it in a very simple experiment.

This renewed attack on the Rochelle salt structure is still in progress, but we do not expect a fully detailed solution. The best that can be hoped for, at least with present data, is that a few major displacements can be detected and tested for reliability. It is difficult to say if sufficient results can be obtained to determine a mechanism for the ferroelectric behavior of the crystal.

Most of what has been said here on Rochelle salt is on the negative side, but it was indicated earlier that some worthwhile results have come out of our studies. These may be summarized as follows:

(1) It has been possible to test and disprove the old hydrogen bond theory of ferroelectricity in Rochelle salt. This was first suggested as a possibility by Beevers and Hughes, and subsequently it received considerable theoretical attention. In this theory it was supposed that hydrogen ordering, somewhat as in KH₂PO₄, took place along the short O_{10} -H···O₁ bond. This would require two of the four bonds of this type in the cell to have an O₁₀-H hydrogen association, and the other two to have an This could have been O_1 -H association. detected easily, but was not.

(2) While most of the hydrogen bond network proposed by Beevers and Hughes was confirmed, one of their bonds was found to be incorrect. The O_8 water molecule had been shown hydrogen-bonded to O_2 and O_6 . We find it bonded O_2 and O_8

(3) We have located the previously undetermined positions of the C-H hydrogens of the tartrate molecule.

(4) One large ferroelectric displacement has been found which we consider to be genuine, and which we believe will prove to be very significant in explaining the ferroelectric properties of the crystal. This involves the orientation of the O_5 hydroxyl group of the tartate molecule. The net hydrogen displacement in the ferroelectric a direction is almost 1Å.

(5) By studying the dependence of the odd (0k0) neutron intensities on irradiation dosage, we have shown that ionizing radiation seriously affects the ferroelectric structure

ture of Rochelle salt. The implications for an X-ray structure analysis have already been discussed, but this result also contributes in a very fundamental way to the understanding of radiation effects in this crystal. The effects on the ferroelectric properties have been studied extensively¹⁴⁾⁻¹⁹⁾, and much of this work has been done here in Japan, so it is perhaps appropriate to present here a brief account of our work.

Most of the explanations that have been offered for the effects of radiation on the ferroelectric behavior of Rochelle salt have been essentially macrostructural in nature. That is, they have not been concerned with the crystal structure, or we could say the microstructure, but rather with locking of the domains by imperfections either induced or reinforced by irradiation. Indeed, there has been good reason for ignoring microstructural changes, since domains are still visible with polarized light long after the hysteresis loop has disappeared-thus indicating that the monoclinic symmetry is retained even after a heavy dose of radiation. The distorted and double loops that are observed after small doses also can be explained on the basis of hindered domain mobility, and hence the domain locking theory has seemed to offer a quite adequate approach to understanding the radiation effects. Nevertheless, there were certain other factors which led us to suspect that this might not be the whole story. The apparent inconsistencies between the neutron and X-ray diffraction data have already been mentioned, but there was also the rather remarkable similarity between the dielectric constant behavior of irradiated crystals and that of crystals containing impurities. It is well known that the ferroelectric properties of Rochelle salt can be greatly altered, and even destroyed, by rather small impurity contents.

Our experiments were very simple. A crystal was subjected to progressive irradiation dosage and the odd (0k0) neutron intensities were measured after each dose. The intensities were found to decrease steadily and eventually seemed to disappear. The first experiments were done with X-irradiation, but because of the large crystals necessary for neutron measurements, we later switched to γ -rays in order to be sure that the damage was dispersed throughout the volume instead of concentrated on the surface layers. The results in both cases were basically the same, and there could be no doubt that microstructural changes were being induced.

Our original purpose had been satisfied, but it seemed worthwhile to look into this problem further. Two rather startling discoveries were made. In the first, a crystal irradiated within the ferroelectric temperature range to the point where the odd (0k0)'s could no longer be detected, was examined optically from about 10° below the lower Curie point to about 10° above the upper one. From the dielectric constant behavior it was expected that the domains would disappear at temperatures above the lower Curie point and below the upper one. Instead, they were visible over the entire temperature range. In the second a similar experiment was done with a crystal irradiated at dry ice temperature. This crystall showed no domains at any temperature.

Our results suggest the following conclusions. There appear to be two basic processes involved when Rochelle salt is irradiated in the ferroelectric phase. One of these is intrinsically microstructural. Whatever the crystal chemical peculiarities of Rochelle salt are that normally cause the monoclinic phase to be stable over its limited temperature range, the damage upsets these stability conditions, and the crystal wants to become orthorhombic. At the same time, however, there is a macrostructural process pinning the domains and introducing monoclinic clamping. The competition between these processes results in locked monoclinic domains, but a decreased spontaneous strain. At low values of the spontaneous strain, as in an unirradiated crystal near a Curie point, the odd (0k0)'s become so weak that they are very difficult to detect. When the crystal is irradiated outside of the ferroelectric range. there are no domains to be locked, and no domain walls to trap damage products, and in this case the microstructural effects do-Thus the crystal remains orthominate. rhombic at all temperatures.

In closing I would like to emphasize that the work that I have discussed on BaTiO₃ and Rochelle salt has come from the combined efforts of several people in addition to myself. Drs. H. R. Danner, R. Pepinsky, and G. Shirane have collaborated on the structure studies. Drs. H. Boutin and F. Jona have collaborated on the irradiation studies of Rochelle salt. Detailed accounts will be published elsewhere under joint authorship.

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DISCUSSION

G. CAGLIOTI In referring to your study of the Ti parameter along the z-direction and the B_{s3} temperature coefficient of Ba, do you think that the values of these parameters would be put in connection of the predictions of Professor Cochran, who states that near the temperature of ferroelectric transition the frequency of the transversal optic normal modes of long wavelength goes to zero?

B. C. FRAZER: Of course our results were not obtained very close to the Curie point. In my case, I do not think our $B_{33}(Ba)$ temperature parameter is sufficiently accurate to make much use of it. Our present value of 0.66 seems quite high when compared with others in the structure, since Ba is quite heavy and this value is the highest in the structure. Furthermore, despite Evans' other difficulties, his Ba temperature parameter should be accurate, and it is only 0.3. We believe that our data may be slightly affected by extinction, and we have started some calculations which show that $B_{33}(Ba)$ becomes smaller with very little change in the other parameters, so that I do not think that very good answer can be given to your question at this time.