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Brief Statement of the Problem

The research done under this contract deals principally with those nuclear relaxation processes in solids which depend on the presence of an electric quadrupole interaction. More specific statements of the problem are given in the original contract and its modifications and in the subsequent sections of this report.

Summary of Results

The results fall into two broad categories, one of which is concerned with the understanding of the various relaxation processes which are encountered, and the other involves the measurement of important physical parameters. While the greatest emphasis was initially placed on the understanding of relaxation processes, probably the most important single result of this research falls into the second of these two categories. This is the measurement of an activation energy which is of importance in connection with deuteron relaxation in hydrogen bonded crystals and which turns out to be of importance also in certain theories of the ferroelectric phase transition. The significance of this connection will be described in detail in later sections of this report.

It will be sufficient at this point to summarize those results that can be described in a few simple sentences. Later sections of the report will then provide a discussion of the background of knowledge into which the results enumerated here may be fitted. The following list provides an outline of most of the accomplishments under this contract:

(a) The determination of the Van Kranendonk enhancement factor γ for Na in NaCl using acoustic excitations of the nuclear spin transitions. The absolute determination rests on the measurement of the acoustic energy density as well as the nuclear spin saturation. The result for the enhancement factor

is $\gamma = \gamma_1 \sim 17$ which is to be compared with $\gamma = \gamma_0 \sim 5$ as calculated for static effects and $\gamma = \gamma_2 \sim 60$ as measured from thermal relaxation for second order processes.

(b) An understanding of the mechanism of spin relaxation of deuterons in KD_2PO_4 . It was found that two distinct spatial motions contribute to the relaxation.

(c) The measurement of the energy parameter ϵ_1 of the Slater-Takagi theory of phase transitions in these crystals. This is the important measurement to which reference was made in the opening paragraph. It is the H_3PO_4 - HPO_4 ion pair formation energy of the Takagi theory. It is also one of the two activation energies associated with the deuteron relaxation.

(d) The verification that the interbond jumps discovered through the study of deuteron relaxation provide the sole mechanism responsible for electrical conductivity in these crystals. The principal basis for the verification is the observation of equal activation energies for the electrical conductivity and one of the processes of deuteron relaxation.

(e) The observation of an arsenic spin resonance in just one case of an AsO_4 group present in a solid. This is in $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$. The arsenic resonance in AsO_4 has not been observed in any other solid, including the case of KH_2AsO_4 , a crystal of primary interest in this research.

(f) The analysis of high temperature proton spin relaxation data in KH_2AsO_4 as due to coupling with a rapidly relaxing arsenic nucleus, and not to spin diffusion to paramagnetic impurity ions as previously reported.

(g) Theoretical extensions of the Slater-Takagi theory of the phase transition in KH_2PO_4 -type crystals which are suggested by the experimental results, and a start on the analysis of consequences of the introduction of long-range electrostatic interactions in addition to the short-range

interactions. Good agreement is obtained between theory and experiment on spontaneous polarization as a function of temperature below the critical temperature T_c , and on susceptibility above T_c .

(h) Numerical results which are new include the following: an activation energy for deuterons of 0.58 ev which describes both the electrical conduction and the jump motion between bonds on which one of the several contributions to spin relaxation depends; an activation energy for deuterons of 0.078 ev describing the jump motion of deuterons from one end of its bond to the other; an electrical conductivity in KD_2PO_4 equal to $0.79 \exp(-0.58 \text{ ev/kT}) \text{ ohm}^{-1} \text{ cm}^{-1}$; i.e. of order $10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature and 10^{-14} at the ferroelectric transition temperature of 213° K ; attenuation of longitudinal sound waves in NaCl at room temperature and 15 Mc/sec. equal to 0.015 cm^{-1} for the amplitude in a sample of good optical quality; and, $\gamma_1 = 17$ for Na in NaCl as mentioned above. In addition, line width data and values of thermal relaxation time for protons, deuterons and other nuclei in a variety of crystals over a range of temperatures extending from 4.2° K to 375° K as a function of frequency and crystal orientation in a magnetic field have been obtained and can be found in the publications listed in this report.

History and Objectives

Work on this contract began on July 1, 1957 following the conclusion of work on Contract AF 18(600)-653 to which it is closely related. The final report on Contract AF 18(600)-653 is contained in AFOSR-TR-58-51 of April 1, 1958. The principal accomplishment under the original contract was the first observation of nuclear spin saturation by acoustic excitations. However, there was no direct measurement of the nuclear spin transition probability and, hence, no reliable measurement of the enhancement factor γ_1 since there

was little more than an order of magnitude determination of the acoustic energy density. The latter problem has long been recognized as an especially difficult one. The development of a method for making this measurement, and its application to the determination of γ_1 for Na in NaCl was consequently one of the objectives of the new contract.

Other objectives arose because of the specific direction our studies had taken and because there is a close connection between the understanding of acoustic excitation processes and the understanding of certain natural relaxation processes. The successful observation in our laboratory of the deuteron resonance in a deuterated sample of potassium di-hydrogen phosphate after a search of several years in other laboratories provided the new impetus. Here we had a case of weak static quadrupole splitting combined with strong dynamic quadrupole effects and it was clearly a case from which much could be learned. Thus, the study of nuclear quadrupole interactions in simple hydrogen bonded crystals together with the study of such interactions in the sodium chloride type cubic crystals seemed to provide a good basis for an overall program. The better understanding of the mechanisms of nuclear relaxation via quadrupole interactions became the central objective.

Thus, the title of the new contract AF 49(638)-92 became "Nuclear Relaxation Times". As stated in the contract, the problem was to study phonon relaxation times, and, in addition, to study nuclear relaxation times in several types of crystals, with and without acoustic excitations, and as a function of temperature, magnetic field, and crystal orientation. The anticipated use of several different kinds of excitation, pulsed, continuous wave, and double frequency was specified. The contract was subsequently renewed on two occasions to provide an overall duration for accomplishing the objectives extending from the initial date of July 1, 1957 to the final

date of September 30, 1962. The restatement of objectives in the renewal agreements had the effect of making the original objectives somewhat more specific, and of introducing the study of the basis for ferroelectricity in hydrogen bonded crystals as a possible outgrowth of the nuclear relaxation studies.

Achievement of Research Objectives

The research accomplished will now be described under four principal headings. Since the published reports on this work are rather complete, and will become more so when papers now being written have also been published, it will be sufficient in this report to describe each topic briefly listing all of the references to theses and publications which provide the more complete description.

1. Ultrasonic Excitation of Nuclear Spin Transitions in a Solid. The primary objective of this phase of the work was to make a quantitative determination of the probability of a nuclear spin transition which is induced by the lattice vibrations. The solid chosen for this study was sodium chloride, and the nucleus was Na^{23} . Nuclear spin transitions were externally induced by an acoustic wave of 15 Mc/sec. via the electric quadrupole interaction between the nucleus and the lattice. The 15 Mc/sec. frequency of the acoustic wave corresponded to the $\Delta m = 2$ resonance frequency of the sodium nucleus in the constant magnetic field of about 6700 gauss to which it was subjected. The quantitative effect of the acoustic wave was measured by comparing the population differences between the relevant spin states in the presence of the acoustic excitation with the population differences in the absence of this excitation.

In order to make an absolute determination of the transition probability, it was necessary to know the energy density (or amplitude) of the acoustic

wave. Since this problem had not previously been solved, the development of a method by which such energy densities could be measured constituted an important subsidiary objective of the experiment. It was in fact the main problem. The method used here was to show that the circumstances of the experiment could be such that the sole contribution to acoustic energy loss from the band of frequencies contained within the nuclear line width was due to acoustic attenuation within the volume of the material, and then to make a precise determination of the attenuation factor. From a knowledge of the attenuation, the acoustic power input to the nuclear sample, and the resultant nuclear spin saturation, a determination of the one experimental parameter on which the strength of the interaction depends, was made. This parameter is the Sternheimer enhancement factor γ_1 . The value obtained here was about three times the value obtained in a previous determination and as expected lies somewhere between the lower value which is relevant for static processes and the higher value which is relevant for higher order processes. It is believed to be the most nearly correct determination that has been made so far. Unfortunately, it has not yet been possible to perform similar experiments on other nuclei or on nuclei in other environments. Also, there is not yet a good theory of the enhancement factor for dynamic processes.

Data on the attenuation of sound in NaCl is a subsidiary result of this experiment. A significant feature of these results is the observation that equally good samples of NaCl which are similar in all respects that have so far been tested (including their optical quality) have values of acoustic attenuation which differ from each other by amounts which lie outside the experimental error. Equally good samples of the same geometry may differ in their values of attenuation by as much as a factor of 15. The only correlation which has been found between the attenuation and any other physical phenomenon

is the observed correlation with the rate of nuclear spin transitions in the presence of a specified amount of acoustic power supplied to the sample. This result tends to confirm the reliability of the methods used for both the measurement of attenuation and the corollary measurement of acoustic energy density. However, it provides no suggestion of the possible causes of different attenuations in samples which are otherwise similar. It is probable that the further study of such causes using nuclear magnetic resonance methods will provide information on microscopic crystalline defects which are difficult to detect in any other way.

A complete report on this research is contained in the Ph.D. thesis of Harold Patterson Mahon, "Acoustic Excitation of Nuclear Spin Transitions in NaCl", University of Washington, Seattle, 1961. A summary of the results on the enhancement factor for the Na nucleus in NaCl was given at the January 1962 meeting of the American Physical Society in New York. An abstract appears in Bull. Am. Phys. Soc. II, Vol. 7, No. 1, 38 (1962).

A separate report on acoustic attenuation in NaCl describing methods and results is being prepared. No further report on enhancement factors will be made until other measurements corroborating the results described here and extending them to other nuclei and other crystals have been made. Plans for such additional measurements have been under consideration for some time.

2. Nuclear Spin Relaxation of Deuterons in the Deuterated Form of KD_2PO_4 . This research began as soon as the deuteron resonance was observed and a nuclear resonance spectrometer of sufficiently low excitation level to prevent excessive spin saturation was successfully constructed. The principal difficulty here was the previously unsuspected long relaxation time of the order of ten minutes of the deuterons in this crystal. The two main objectives of the program which was started as soon as the deuteron resonance was

observed were: (a) Determination of the static electric field gradient tensor components at the site of the deuteron; and, (b) Observation of the deuteron relaxation time and interpretation in terms of deuteron dynamical processes. The first of these objectives was easily achieved. Since the deuteron resonance line width of the order of 0.7 kc/sec. is small compared with the electric quadrupole splitting frequencies of the order of 200 kc/sec. the various lines in the deuteron spectrum were easily resolved at all angles of crystal orientation in a magnetic field. Using the well-known theory of electric quadrupole splitting it was not difficult to determine the orientation of the principal axis system of the electric field gradient tensor and the magnitude of the tensor components. The main results may be summarized as follows: The principal axis of the tensor lies along the direction of the hydrogen bond, the magnitude of the coupling constant e^2Qq expressed in frequency units is 119.5 kc/sec., and the asymmetry parameter is $\eta = 0.049$. The research is fully described in:

Ph.D. thesis of John Ludwig Bjorkstam, "Deuteron Magnetic Resonance Spectrum and Relaxation in KD_2PO_4 ", University of Washington, Seattle, 1959. It is also described in a technical report, AFOSR TN 58-996, AD No. 205-902, January 15, 1959 and in an article, Phys. Rev. 114, 961 (1959).

The second objective was not completely achieved until after much more study. Bjorkstam had observed strange saturation effects which pointed to an interchange of deuterons between neighboring hydrogen bonds but which were otherwise unexplained. Also, he had observed a strong anisotropy in the relaxation time which was partially explained by a particular model of relaxation, which failed, however, to give simultaneously a correct description of the dependence of relaxation on temperature and magnetic field. It wasn't until after it was recognized that there are two principal mechanisms of relaxation in this crystal that a correct description fulfilling all of the

conditions was possible. Thus, competing mechanisms were postulated, tested, and eventually verified. The main features are: (a) Deuteron jump motions between bonds which effectively interchange deuterons in distinct bonds at a rate corresponding to life times in a bond which depend exponentially on the reciprocal of the temperature over an extended range of temperatures; and (b) a jump motion between two equilibrium points within a bond which is also exponentially dependent on the reciprocal of the temperature. As a consequence of the two kinds of jump motions there are changes in the electric field gradient tensor components as seen by the deuterons which cause relaxation. When the two relaxation rates are added to the rate which is contributed by a third mechanism, the spin diffusion mechanism, one obtains a total rate which can be checked for its dependence on all parameters, temperature, frequency and crystal orientation. The check was made and the postulated mechanisms were verified to a very high degree of certainty. As a consequence, it can be asserted that the relaxation mechanisms for deuterons in crystals of the type under consideration are quite well understood.

As initial objectives the determinations of electric field gradient tensors and the understanding of relaxation processes appeared to be sufficiently ambitious to justify whatever restriction such limitation of specified objectives may imply. As is so often the case, however, there are consequences of the new knowledge which were previously not anticipated. The important consequences of the present study appear to be: (a) A new concept of the hydrogen bond possessing an asymmetric potential well for its associated proton or deuteron, even in the absence of an electric field, and an activation energy for the jumping of the potential minimum from one side to the other of the bond center; and, (b) an indirect measurement of changes in the electric field gradient tensor due to jumps from one side of the bond

to the other. As will be described later, the first consequence has implications with regard to the nature of the ferroelectric phase transition, and the measured activation energy can be inserted as the numerical value of a parameter appearing in one of the theories of such transitions. The second consequence is of less immediate interest since our knowledge of the sources of electric field gradients in crystals is still incomplete. However, when such theories have been more fully developed, measurements of the type made here may prove to be quite useful in the comparisons between theory and experiment.

The results of these studies on deuteron relaxation, excluding however the subsequent work on the connection with ferroelectricity, is contained in a thesis, an article in *The Physical Review*, and a series of abstracts of papers given at meetings of The American Physical Society. Specific references are:

Ph.D. thesis of V. Hugo Schmidt, "Deuteron Jumping in KD_2PO_4 ", University of Washington, Seattle, 1961; an article on essentially the same subject, *Phys. Rev.* 126, 447 (1962); and the following abstracts, *Bull. Am. Phys. Soc.* II, Vol. 2, No. 8, 383 (1957); Vol. 4, No. 8, 462 (1959); Vol. 5, No. 5, 345 (1960); and Vol. 5, No. 7, 497 (1960). In addition, a report of a preliminary study of the deuteron spectrum in Rochelle Salt is contained in *Bull. Am. Phys. Soc.* Vol. 5, No. 5, 345 (1960).

The thesis contains also a full account of the connection between the measured activation energy for jumps between bonds and the measured electrical conductivity. In order to establish this connection, reliance could not be placed on the rather meagre data on electrical conductivity which was previously available, especially since it is the deuterated form of the crystal with which we are now dealing. Consequently, a program of electric conductivity measurements was started. It was established that the temperature dependence

of the electrical conductivity and the temperature dependence of that part of the deuteron relaxation which was due to interbond jumps were governed by precisely the same activation energy over the entire available temperature range above the Curie temperature of 213° K. Also, it was shown by collection of the liberated gases in electrical conduction that the heavy ion motion is in fact the sole contributor to electrical conductivity. However, an attempt to make Hall Effect measurements on the heavy ion carrier in order to measure separately the density of the carriers failed. A separate study of heavy ion mobilities and defect densities has subsequently been initiated and work along these lines is in progress.

3. The Relaxation of Spin $1/2$ Nuclei. Since the diffusion of energy to paramagnetic impurity ions is a relaxation mechanism which may be dominant (as for the protons and phosphorous nuclei in KH_2PO_4) or merely contributory (as for the deuterons in KD_2PO_4) a better understanding of this mechanism appeared to be important. The primary objective here was to be able to subtract from the total relaxation rate of deuterons in these crystals that part which was due to spin diffusion and to be able to do this correctly under the various conditions of temperature, frequency and crystal orientation. However, a secondary objective developed when it was found that the observed data were inconsistent with the theory of spin diffusion processes in several respects. The description of these inconsistencies can be based on the following brief summary of the facts.

Spin $1/2$ nuclei are known to relax by a spin diffusion mechanism which carries the spin energy to the electron of a paramagnetic ion which is always present in the crystal. The rate of the relaxation depends of course on the density of the impurity ions. Competing mechanisms may exist if the spin in question is closely coupled to other nuclei in which case one can

also have relaxation by a cross-relaxation process or as a consequence simply of rapid spin motion of the adjacent nucleus due to strong mechanisms of relaxation possessed by the second nucleus. No such competing mechanisms were known to exist in the KH_2PO_4 type crystals, and it was in fact presumed that no such mechanisms were present. One additional fact that is relevant in this discussion is the prediction of spin diffusion theory that there are two limiting cases of such relaxation in one of which the relaxation is limited by the rate of spin diffusion and in the other it is limited by the rate at which the impurity electron can take up the nuclear spin energy. These two limiting cases are known respectively as the slow diffusion case and the fast diffusion case. The theory predicts that both of the two limiting cases should be easily realized in nature and that one should be able to pass easily from one to the other by suitable changes in temperature or magnetic field or both.

The experimental facts at the beginning of this study with regard to protons (and other spin 1/2 nuclei) in KH_2PO_4 type crystals were as follows: In all samples of KH_2PO_4 the protons and phosphorous nuclei relax in a way which is consistent with the predictions of spin diffusion theory in the limiting case of slow diffusion for all temperatures greater than 77° K. On the other hand, the protons in KH_2AsO_4 showed an entirely different behavior. The principal features are a very sharp maximum in the relaxation rate at the Curie temperature and a dependence of relaxation on frequency and temperature above temperatures of about 250° K which looked like spin diffusion relaxation in the limiting case of fast diffusion. In fact the results were so interpreted at the beginning, and some confidence in the interpretation arose because the assumed values of the physical parameters required to make the comparison quantitative (including the electron relaxation rate and its dependence on temperature) were entirely reasonable. Unfortunately, the

values of these parameters could not be checked at that time by an independent measurement.

Three distinct facts contained in the above statements led to the decision to make a more thorough investigation of spin diffusion relaxation and its possible competing processes. One of these was the previously mentioned need to separate the spin diffusion contribution to deuteron relaxation from its other mechanisms. A second stimulus was the completely unexplained result that proton relaxation in samples of KH_2AsO_4 goes through a sharp maximum at the ferroelectric Curie temperature. The third fact was the eventual realization that the proton relaxation at higher temperatures could not be a fast diffusion limiting case of spin diffusion since this assumption is equivalent to the statement that the coupling constant of the electron to the nuclei is small in a certain sense whereas the simultaneous evaluation of parameters which enter into this coupling constant showed that it is approximately as large as it can possibly be.

For all of these reasons, a program of studies of the spin diffusion mechanism was started. We will deal here with only the first portion of this program which was to obtain as much relaxation data as possible on all of the spin $1/2$ nuclei in the various isomorphs of KH_2PO_4 over a large range of temperatures and magnetic fields and wherever possible to provide an interpretation. The measurements included also the small concentration of protons in KD_2PO_4 and by extrapolation they were applicable to the deuterons as well.

The principal conclusions from these studies were:

(a) With the exception of isomorphs containing arsenic, spin $1/2$ nuclei relax by the spin diffusion process in the limiting case of slow diffusion at all temperatures within the range of 4.5° K to 375° K .

(b) The relaxation of the proton in KH_2AsO_4 is probably by spin diffusion at 4.5°K but at all other temperatures the relaxation processes are dominated by effects which arise due to coupling with a rapidly relaxing arsenic nucleus.

Models of relaxation due to coupling with arsenic have been provided, but they have not been checked. The first attempt at a check depended on the results of a search for the arsenic resonance. Because of its importance, considerable effort was put into the search for this resonance. All known techniques were used, and various spectrometers designed especially for this purpose were employed. The various types of transitions were looked for separately. All of these efforts proved to be of no avail, and it was decided that the corroborative evidence which was desired would have to be found in other types of experiments, as, for example, acoustic excitations. Studies along these other lines will be the subject of later reports.

The search for the arsenic resonance had several interesting subsidiary consequences. In order to better understand the conditions under which the arsenic resonance might tend to disappear because of line broadening and other causes, a number of arsenic containing substances, including liquids were studied. Both nuclear magnetic resonance and pure quadrupole resonance techniques were used and the spectrometers were of both the marginal oscillator and self-quenching superregenerative types. Several new resonances were discovered. The most interesting was the first pure quadrupole resonance in a solid involving the AsO_4 group. The observed resonance was at 44.2 Mc/sec . in $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (sodium arsenate) at room temperature. The successful observation of a pure quadrupole arsenic resonance in the AsO_4 group when only one proton is attached, and the failure up to now to observe a similar resonance when two protons are attached (as in KH_2AsO_4) is regarded as significant.

One additional type of study which has been completed falls into the category of spin $1/2$ nuclei. This is the second moment and line shape of the proton resonance in these crystals. The principal motivation for this investigation was the existence of a misconception based on early reports from other laboratories that a line width transition exists at some critical temperature, and that the existence of this transition may be used as a basis for certain theories of ferroelectricity. Since we observe no such transition it seemed important to set the record straight and to show precisely what the line shape is at various temperatures. At the same time a detailed comparison based on calculations using Van Vleck's second moment formula was made. The agreement between theory and experiment was very good. Also, a small effect on the line shape due to slowly relaxing phosphorous nuclei, but absent in the isomorphs containing arsenic, was pointed out and used as corroborative evidence that the arsenic is in fact relaxing rapidly.

A comprehensive account of all of these investigations is given in:

Ph.D. Thesis of Eric Daniel Jones, "The Relaxation of Spin - $1/2$ Nuclei in KH_2PO_4 Type Crystals", University of Washington, Seattle, 1962. In addition, specific reports on the arsenic resonance in AsF_5 , the antimony resonance in SbCl_5 and the arsenic resonance in solid sodium arsenate have been published in J. Chem. Phys. 36, 1690 and 1691 (1962). The paper on the absence of line width transitions was published in J. Chem. Phys. 37, 469 (1962). There was also a paper on a new development in Zeeman modulation for nuclear quadrupole resonance spectroscopy which was published in Rev. Sci. Instr. 33, 775 (1962). Finally, a series of reports to meetings of the American Physical Society have abstracts which have been published in Bull. Am. Phys. Soc. II, Vol. 3, No. 3, 166 (1958); Vol. 3, No. 5, 318 (1958); Vol. 5, No. 7, 498 (1960); Vol. 7, No. 7, 483 (1962). The last reference

contains two abstracts, one on the high temperature proton relaxation in KH_2AsO_4 and the other on a particular aspect of the search for the arsenic resonance.

4. The Phase Transition in Hydrogen Bonded Ferroelectric Crystals.

The study of the implications of these measurements for the theory of ferroelectricity and the further understanding of the phase transition was not given as an objective in the statement of the original contract because such implications were unsuspected. However, it appears that the experimental results have a direct bearing on the theory, and they may in fact assist the further development of the theory. The main implications are of two kinds. As already mentioned in the section on deuteron relaxation, these measurements suggest a rather definite point of view which should be taken in regard to the nature of the hydrogen bond as an entity the properties of which are strongly determined by the local environment, for example, the lattice vibrations. The second implication is of greater immediate practical importance. This is the possible connection between the activation energy measured in the deuteron relaxation experiments and associated with the jump motion of the deuteron from one side to the other of its bond and an energy parameter which appears in the Takagi modification of the Slater theory of ferroelectricity in these crystals which is associated with the production of a $\text{H}_3\text{PO}_4 - \text{HPO}_4$ ion pair. According to the Takagi theory, the steepness of the slope of the spontaneous polarization curve below the Curie temperature is a sensitive function of the ratio of this energy, which is denoted as ϵ_1 , and another energy called ϵ_0 . The latter energy is very precisely defined in the theory, but its magnitude is very nearly equal to kT_c where T_c is the Curie temperature. According to the measurements on deuteron relaxation together with the assumption that it is in fact the energy ϵ_1 which is being measured we obtain the result that the ratio ϵ_1/ϵ_0 is equal to 5.9. It turns

out that this ratio when inserted into the Takagi theory, also provides the best fit between the experimental polarization curve as a function of temperature and the prediction of the theory. A change of 20% in either direction makes the theoretical curve depart radically from the observed curve. This is a remarkable result and appears to be worthy of considerable further investigation. For this reason the theory has been and will continue to be studied extensively. The implications of the Takagi theory with respect to the specific heat and the high temperature susceptibility have been investigated, and additional energy parameters have been introduced. As is to be expected, the requirements on the theory become more stringent as the theory is asked to encompass a greater range of physical phenomena. Consequently, it is not surprising that the initial success obtained when only the spontaneous polarization was being studied, are not being duplicated as additional steps are taken. However, the program of study which is now going on and which was stimulated by the results of the nuclear resonance measurements is undoubtedly of considerable value.

The only public reports on this contribution to understanding of the ferroelectric phase transition are contained in a brief reference in Phys. Rev. 126, 447 (1962); a post deadline paper on "Experimental Support for a Modified Slater Theory of Ferroelectricity in KH_2PO_4 Type Crystals" at the meeting of the American Physical Society, Berkeley, December 29-31. (1960); an invited paper on "Ferroelectricity in KH_2PO_4 Type Crystals" at the meeting of the American Physical Society, Monterey, March 20-23 (1961); and a series of lectures by the writer of this report at the Summer Institute of Theoretical Physics in Boulder, Colorado, Summer 1962. The lectures will be published, but the publication is not yet available. In addition, a paper on this subject dealing with the combined consequences of short range and long range forces and based quantitatively on the deuteron relaxation measurements is being

prepared for publication. As it now stands, the only serious discrepancy between theory and experiment is in the transition heat. As a consequence, new measurements of the specific heat are being made in this laboratory.

Educational Objectives

Important educational objectives have been achieved simultaneously with the accomplishment of research results. One consequence has been the development of a research laboratory capable of continued work along the lines which have been initiated. As a consequence of the support obtained under this contract, we now have a larger and better equipped magnetic resonance research laboratory than would have been possible otherwise.

Educational achievements under the contract are perhaps most effectively summarized by listing the various students who have been granted advanced degrees while doing research supported by the contract. The Ph.D. students, the date of granting their degrees, and their present location are as follows:

John L. Bjorkstam, 1958, Associate Professor, Department of Electrical Engineering, University of Washington.

V. Hugo Schmidt, 1961, Professor of Physics, Valparaiso University, Indiana.

Harold P. Mahon, 1961, Research Professor, University of Colorado, Boulder, Colorado.

Eric D. Jones, 1962, Research Staff, Bell Telephone Laboratories, Summit, New Jersey.

The students to whom M.S. degrees were granted while working on the contract are:

George H. Bloom	1959
William H. Coop	1960
Henry Minglo Ho	1961
William L. Barrett	1961

Robert Wu	1962
Jon Soest	1962
Vaclav Kostroun	1963

Summary on Publications

The various publications fall into the categories of Ph.D. Theses, AFOSR Technical Reports, articles in journals of the Physical Societies, and abstracts of talks at meetings of the American Physical Society.

All of the publications have been listed above. They are listed again for easy reference.

1. Ph.D. Theses, University of Washington, Seattle

John L. Bjorkstam, "Nuclear Magnetic Resonance in Potassium Dihydrogen Phosphate Type Crystals".

V. Hugo Schmidt, "Deuteron Jumping in KD_2PO_4 ".

Harold P. Mahon, "Acoustic Excitation of Nuclear Spin Transitions in $NaCl$ ".

Eric D. Jones, "The Relaxation of Spin - 1/2 Nuclei in KH_2PO_4 Type Crystals".

2. AFOSR Technical Reports

John L. Bjorkstam and Edwin A. Uehling, "The Deuteron Magnetic Resonance Spectrum and Relaxation in KD_2PO_4 ", AFOSR TN 58-996, January 15, 1959.

3. Articles

John L. Bjorkstam and Edwin A. Uehling, "Deuteron Magnetic Resonance Spectrum and Relaxation in KD_2PO_4 ", Phys. Rev. 114, 961 (1959).

V. Hugo Schmidt and Edwin A. Uehling, "Random Motion of Deuterons in KD_2PO_4 ", Phys. Rev. 126, 447 (1962).

Eric D. Jones and Edwin A. Uehling, "Nuclear Magnetic Resonance of Arsenic and Antimony in Liquid AsF_5 and $SbCl_5$ ", J. Chem. Phys. 36, 1691 (1962).

3. Articles (cont'd)

Eric D. Jones and Edwin A. Uehling, "Nuclear Quadrupole Resonance of As^{75} in $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ", J. Chem. Phys. 36, 1691 (1962).

J. L. Bjorkstam, E. D. Jones, H. B. Silsbee and E. A. Uehling, "Absence of a Linewidth Transition for the Protons in KH_2PO_4 Type Crystals", J. Chem. Phys. 37, 469 (1962).

Eric D. Jones, "Zeeman Modulator for Nuclear Quadrupole Resonance Spectroscopy", Rev. Sci. Instr. 33, 775 (1962).

4. Abstracts

John L. Bjorkstam and Edwin A. Uehling, "Deuteron Magnetic Resonance in KD_2PO_4 ", Vol. 2, No. 8, 383 (1957).

John L. Bjorkstam and Edwin A. Uehling, "Nuclear Spin-Lattice Relaxation in KH_2PO_4 ", Vol. 3, No. 3, 166 (1958).

Edwin A. Uehling and John L. Bjorkstam, "Frequency Dependence of the Nuclear Spin-Lattice Relaxation", Vol. 3, No. 5, 318 (1958).

V. Hugo Schmidt and Edwin A. Uehling, "Jumping Rate of Deuterons between Hydrogen Bonds of KD_2PO_4 ", Vol. 4, No. 8, 462 (1959).

John L. Bjorkstam and Edwin A. Uehling, "Deuteron Magnetic Resonance Spectrum in Deuterated Rochelle Salt", Vol. 5, No. 5, 345 (1960).

Edwin A. Uehling and John L. Bjorkstam, "Domain Effects in the Deuteron Magnetic Resonance Spectrum of KD_2PO_4 ", Vol. 5, No. 5, 345 (1960).

V. Hugo Schmidt, Henry B. Silsbee and Edwin A. Uehling, "Nuclear Spin-Lattice Relaxation Mechanisms for D in KD_2PO_4 ", Vol. 5, No. 7, 497 (1960).

Eric D. Jones, Henry B. Silsbee and Edwin A. Uehling, "Nuclear Spin-Lattice Relaxation by Spin Diffusion to Paramagnetic Ions in KH_2AsO_4 ", Vol. 5, No. 7, 498 (1960).

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