The Piezoelectric, Dielectric, and Elastic Properties of $ND_4D_2PO_4$ (Deuterated ADP)

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Measurements of the dielectric constants, piezoelectric constants, and elastic constants have been made for the crystal $ND_4D_2PO_4$ (heavy water ADP). This crystallizes in the same form as normal ammonium dihydrogen phosphate (ADP) but has a transition at $-31°C$ which is 94° higher than that for normal ADP. From the form of the crystal below the transition temperature, it is inferred that the transition is an antiferroelectric one with one of the "*a*" crystallographic axes as the antiferroelectric axis. The crystal has a zero temperature coefficient of frequency at 0°C, and it may be of use in transducers and mechanical filters.

I. INTRODUCTION

WHEN ammonium dihydrogen phosphate (ADP) is cooled down to $-125°C$ (148°K), a transition occurs which produces a large enough change in volume to shatter the crystal. Dielectric and piezoelectric measurements[1,2] show that the transition is not a ferroelectric transition. On the other hand, the specific heat anomaly[3] is large enough to indicate an order disorder transition. It was generally believed[1,2] that this transition was due to an interaction of the NH_4^+ ions due to their deviation from a spherical symmetrical configuration. However, the specific heat anomaly occurring at this transition is much larger than those observed in other ammonia transitions.

Recently,[4] however, all the hydrogens in the crystal have been replaced by deuterium making the crystal $ND_4D_2PO_4$. The crystal had the same tetragonal structure as ADP, but the transition temperature was shifted from 148°K to 242°K ($-31°C$) an increase of 94°C. This result shows that the transition cannot be an ammonia transition like NH_4Cl, for instance, which changes the transition temperature by only a few degrees, when the hydrogens are replaced by deuterium. From the specific heat data[3] the transition is believed to be an order-disorder transition in the X_2PO_4 (X=H or D) groups, and from the change in crystal structure discussed below it is believed that the crystal goes into an antiferroelectric state below the transition temperature.

In the ferroelectric crystal potassium dihydrogen phosphate (KDP), the crystal changes from tetragonal to orthorhombic form on lowering the temperature through the transition temperature, with the new *a* and *b* axes at 45° from the high temperature *a* axes. This shift of the crystal axes is caused by the piezoelectric strain produced by the spontaneous polarization. For $ND_4D_2PO_4$, as shown by the x-ray and optical work of Dr. E. A. Wood, the structure is orthorhombic below the transition temperature, with the low temperature *a* and *b* axes coinciding with the high temperature *a* axes. The most sensitive test is an optical one, which shows that the crystal has become biaxial in a (100) plane with the two optic axes ±9° from the *Z* axis.[5] It appears that the crystal structure change accompanying the transition in $NH_4H_2PO_4$ and $ND_4D_2PO_4$ is caused by a quadratic distortion proportional to squares and even powers of the spontaneous polarization, and hence the structure is antiferroelectric.

A phenomenological development of this effect is given in a companion paper which makes it appear probable that the antiferroelectric axis lies along one of the *a* (*x* or *y*) crystallographic axes. This agrees also with the x-ray data and makes it appear probable[5] that, below the transition temperature, the hydrogen nuclei take the form of the pattern shown by Fig. 1, which is an antiferroelectric arrangement with the antiferroelectric axis along one of the original *a* crystallographic axes.

Dielectric, piezoelectric, and elastic measurements have been made over temperature ranges down to the transition temperature. Without protection, the crystal fractured below the transition temperature due to the large volume distortion effects, and no measurements

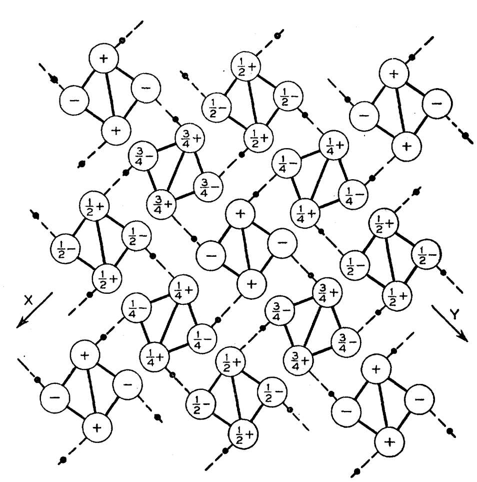

FIG. 1. Arrangement of hydrogen nuclei to produce an antiferroelectric condition.

[1] W. P. Mason, Phys. Rev. **69**, 173 (1946).
[2] Baertschi, Matthias, Merz, and Scherrer, Helv. Phys. Acta **18**, 238 (1945).
[3] C. C. Stephenson and A. C. Zettlemoyer, J. Am. Chem. Soc. **66**, 1405 (1944).
[4] B. T. Matthias, Phys. Rev. **85**, 140 (1952).
[5] Wood, Merz, and Matthias, Phys. Rev. **87**, 544 (1952).

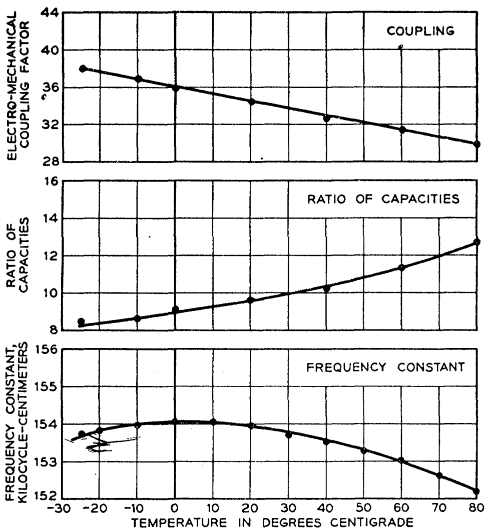

FIG. 2. Properties of a 45°Z cut crystal.

could be made of the elastic and piezoelectric constants below the transition temperature. Above the transition temperature, the elastic constants have a very small variation with temperature, and Fig. 2 shows the frequency temperature variation, the ratio of capacities, and the electromechanical coupling factor for one of the principal cuts—the 45° Z cut, which has been used considerably in underwater sound equipment. The temperature coefficient of frequency is quite low, and the piezo-

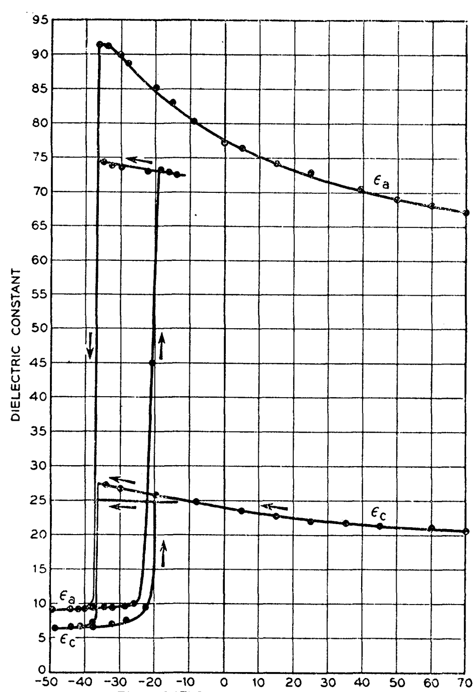

FIG. 3. Dielectric constants along a and c axes showing drop at transition temperature.

electric and dielectric constants are about 50 percent larger than for normal ADP. Hence, it appears that such crystals may have practical applications in electromechanical transducers and in mechanical wave filters. The extra cost of the deuterium can be minimized by saving all cuttings and returning them to the growing bath. The difficulty of cracking at the transition temperature can be overcome by introducing a small amount of thallium[2] or rubidium, both of which have been found to prevent cracking in normal ADP.

II. MEASUREMENTS OF THE ELASTIC, PIEZOELECTRIC, AND DIELECTRIC CONSTANTS OF $ND_4D_2PO_4$

All of the elastic, dielectric, and piezoelectric constants of ADP and $ND_4D_2PO_4$ can be determined from seven oriented cuts by measuring the dielectric con-

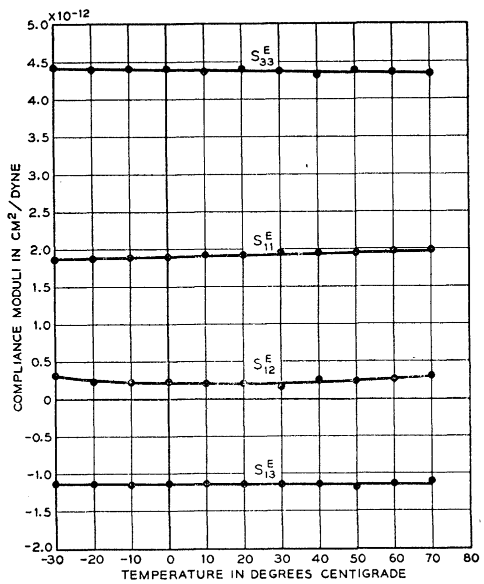

FIG. 4. Elastic compliances s_{11}, s_{33}, s_{12}, and s_{13} as a function of temperature.

stants, the resonant and antiresonant frequencies. Since this process has been described[1] in connection with measurements for normal ADP, only the measured results will be presented. The cuts were obtained from a small sized crystal grown from a saturated solution by continuously dropping the temperature.

Figure 3 shows a measurement of the dielectric constant along the a and c (x and z) axes for a crystal covered with a coat of plastic cement. Above the transition point the dielectric constant along both axes increases as the temperature is decreased down to a definite temperature below which the dielectric constant suddenly drops to a low value. With a plastic coating this temperature is about -37°C, whereas for a free crystal it is about -32°C. The value along the a axis becomes about 9.0, while along the c axis it is about

6.5. On raising the temperature the dielectric constant suddenly increases to nearly its high temperature value at about −20°C. Without coating this temperature is −26°C. This transition can be made to occur repeatedly by temperature cycling.

As shown in the companion paper, there should be three independent dielectric constants below the transition temperature. Since one does not know which *a* axis will become antiferroelectric, two pieces were first tried, one an *x* cut and the other a *y* cut. On taking them below the transition temperature, they had identical dielectric constants. It appears that the mechanical bias put on by the holder determines the direction of the antiferroelectric axis. Next a square piece with two sets of electrodes along the *x* and *y* axes was measured, and it appeared that below the transition temperature one had about 25 percent larger dielectric constant than the other. However, the capacity for this arrangement dropped to such a low value that the measurements were not very reliable.

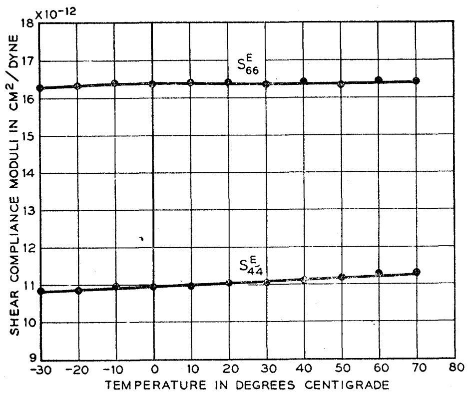

FIG. 5. Shear elastic compliances s_{44} and s_{66} as a function of temperature.

The six elastic compliance moduli are shown by Figs. 4 and 5. Comparing these with similar values for normal ADP,[1] we see that the values are not much changed but the temperature coefficients are much improved. For the two principal cuts, the 45° *Z* cut and 0° *Z* cut shear mode, zero temperature coefficients of frequency are found.

The two piezoelectric constants are shown by Fig. 6. The principal constant is the d_{36} piezoelectric constant, and this is increased 50 percent over that for normal ADP. Hence, it requires only two-thirds the voltage gradient applied to give a determined piezoelectric displacement, and for a given power output from a transducer there is less chance for a voltage breakdown. The other constant d_{14} is about 5 times as large in $ND_4D_2PO_4$ as in normal ADP but is still not large enough to be very useful.

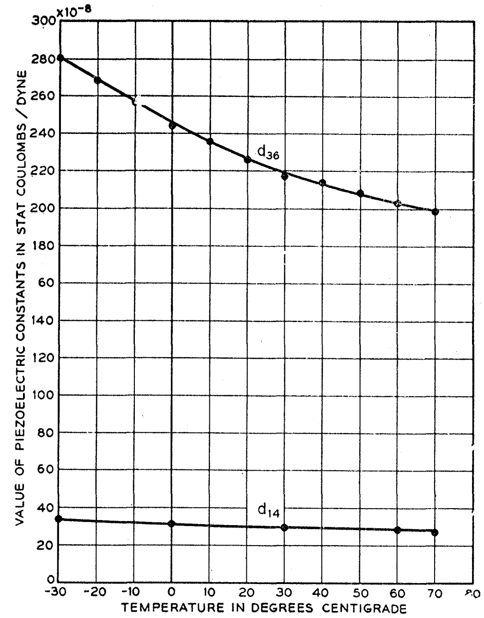

FIG. 6. Piezoelectric constants d_{14} and d_{36} above the transition temperature.

III. DISCUSSION OF RESULTS

Ammonium dihydrogen phosphate and the modification with deuterium $ND_4D_2PO_4$ are interesting technically, due to the large piezoelectric constant and the high electromechanical coupling factor together with freedom from dehydration effects and relatively good mechanical properties. The deuterium modification should be capable of producing more power for the same breakdown voltage gradient. The added frequency-temperature stability may be useful in such devices as mechanical filters which have to remain frequency-stable over a wide temperature range.

On the theoretical side, these crystals are of interest owing to their antiferroelectric properties. The discontinuity[3] in the specific heat is large enough to indicate an order disorder transition which is associated with the ordering of the positions of the hydrogen or deuterium nuclei in an antiferroelectric arrangement below the transition temperature. This interpretation is confirmed by the change in the unit cell from tetragonal to orthorhombic with the low temperature axes coinciding with the high temperature axes.

Note added in proof:—Since this paper originally went to press, a private communication has been received from Professor R. Pepinsky stating that he has a typewritten copy of a paper by Takeo Nagamiya of Osaka University, Japan, entitled "On the Theory of the Phase Transition and the Dielectric, Piezoelectric, and Elastic Behavior of $NH_4H_2PO_4$, I," in which this theory of antiferroelectric behavior is stated, with figures drawn, illustrating the proposed structure.