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Order-Disorder Model Theory for the Ferroelectric Effect in the Dihydrogen Phosphates

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A term in polarization energy is added to the Slater-Takagi model of ferroelectricity in $KH_2PO_4(KDP_H)$. This free-energy function relates the shift in Curie point temperature due to deuteration of the compound with the measured change in saturation spontaneous polarization. The dielectric constant ϵ_c obtained by numerical differentiation of the free-energy function has sharp maximum at the Curie temperature. With a change of parameters, the model also reproduces some of the details of antiferroelectric behavior.

INTRODUCTION

THE ferroelectric effect in potassium dihydrogen phosphate (hereafter KDP_H) and its isomorphic compounds has been the subject of extensive experimental and theoretical investigation. For the compounds which are ferroelectric, it has been determined that there is a second order transition at the Curie temperature,[1] and that the substitution of deuterium for hydrogen in compounds results in significant changes in both Curie temperature and saturation spontaneous polarization.[2,3] The temperature dependence of dielectric constant in the polarization direction is similar to other ferroelectrics in that a sharp maximum occurs at the Curie temperature.[4] Neutron diffraction has shown that below the Curie temperature there is an ordering of protons on the hydrogen bonds of the crystal; above the transition these protons go into a disordered state.[5] On the other hand, ammonium dihydrogen phosphate (ADP_H) which has a similar structure shows antiferroelectric properties.[6,7] That is, the dielectric constant has a Curie law temperature dependence, but the material exhibits no spontaneous polarization.

Proposals of model theories for the ferroelectric effect may be generally divided into two categories. The models of Mason[8] and Pirenne[9,10] neglect near-neighbor interactions and consider that the phenomenon is essentially the result of Boltzmann distribution of the protons between two energy levels. The separation of these levels is determined primarily by the field due to the polarization of the crystal and, therefore, indirectly by the distribution of protons in the two levels. In general, it may be said that with the framework of their assumptions as to the microscopic details of the mechanism, these theories are able to explain a large number of the ferroelectric phenomena. However, there are two notable exceptions: (1) The break in the curve of spontaneous polarization vs temperature[3] is significantly sharper than the theories predict; and (2) These theories would seem to predict that ammonium dihydrogen phosphate would also be ferroelectric, since it has the same crystal structure. There appears to be no simple way of modifying these theories to explain antiferroelectric behavior.

On the other hand, the order-disorder model first presented by Slater[11] and modified by others[12,13] neglects long-range dipole-dipole forces and concentrates its attention on near-neighbor interactions. This type of model presents no basis for the explanation of the Curie temperature shift due to deuteration of the crystal and, secondly, up to the present time, has not provided a description of the dielectric properties in the ferroelectric region.

The model described in this paper considers both types of interactions and shows that the two previous classes of models are essentially complementary.

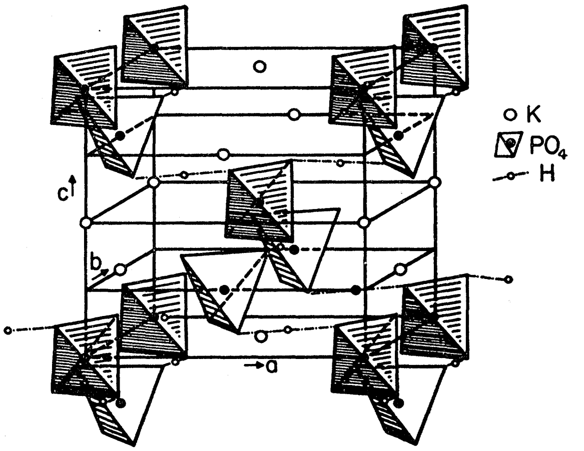

FIG. 1. The crystal structure of KDP [after J. West, Z. Krist. 74, 306 (1930)].

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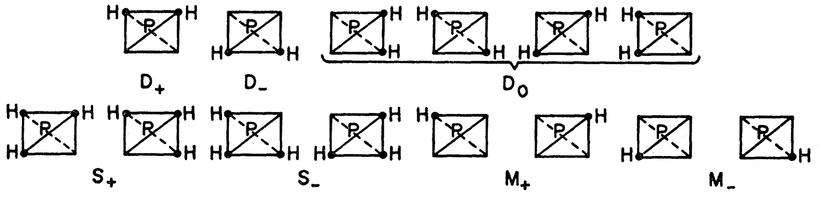

FIG. 2. Phosphate radical configurations.

LONG-RANGE, SHORT-RANGE FORCE MODEL

The crystal structure of $\mathrm{KDP_H}$ is shown in Fig. 1. This paper will be primarily concerned with the behavior of the sytem of phosphate radicals and the hydrogen bonds which connect them to form a three-dimensional network. There are a number of possible hydrogen-phosphate radical configurations. With the exception of those with four or no hydrogens near a particular $\mathrm{PO_4^{-3}}$ radical, these are presented in Fig. 2. Slater[11] based his order-disorder model on a free-energy function which considered only the configurations D_+, D_-, and D_0. He was able to describe the number of possible arrangements of the crystal (and therefore the entropy) as a function of the number of radicals in each of these configurations. He completed his free-energy function by assigning a higher energy ϵ_0 to the configuration D_0. A major defect of this theory was its prediction of a first-order transition at the Curie point. Takagi[12] removed this objection when he considered all the configurations shown in Fig. 2, and assigned a higher energy ϵ_γ to the configurations M_+, M_-, S_+, and S_-. The inclusion of these configurations with other than two protons allows for the possibility of proton transfer from one radical to the next and the violation of local neutrality. It appears that this mechanism can be represented to a good approximation without considering the higher energy configurations with four and no protons. However, neither of these theories contained the basis for the explanation of the effect of deuterium substitution on the Curie temperature. They also contained Slater's assumption that the self-polarization energy of the crystal is not altered by the transition to the paraelectric phase. The present model removes this assumption by considering the self-polarization energy in its free-energy function. We shall assume that the energy of polarization A_p is represented by

$$A_p=\epsilon_\alpha(D_+-D_-+\tfrac{1}{2}M_+-\tfrac{1}{2}M_-+\tfrac{1}{2}S_+-\tfrac{1}{2}S_-)\times(D_+-D_-+\tfrac{1}{2}M_+-\tfrac{1}{2}M_-+\tfrac{1}{2}S_+-\tfrac{1}{2}S_-+E), \quad (1)$$

where M and S dipoles are assigned one-half the magnitude of the D_+ and D_- dipoles. E is an applied external field expressed in terms of a number of D_+ dipoles. ϵ_α is essentially an energy per $(\text{molecule})^2$. A_p may be interpreted in the following fashion. The last term represents contributions to the field at a particular dipole from other dipoles in the crystal and from the external applied field. The interaction energy is then obtained by multiplying this term by the first term in parentheses which is a summation over all dipoles in the crystal.

FREE-ENERGY FUNCTION

Our free-energy function may be written as

$$A=A_p+D_0\epsilon_0+(M_++M_-+S_++S_-)\epsilon_\gamma-kT\ln W, \quad (2)$$

where, following Takagi, we write

$$W=\frac{b_+{}^{b+}b_-{}^{b-}}{(b_++b_-)^{(b_++b_-)}}\frac{4^{D_0}2^{(M_++M_-+S_++S_-)}N!}{D_+!D_-!D_0!M_+!M_-!S_+!S_-!}; \quad (3)$$

b_+ is the number of bonds/mole which have their hydrogens placed so as to contribute to a plus polarization; b_- corresponds to bonds contributing a minus polarization. These may be expressed as simple functions of the phosphate configurations.

$$b_+=(2D_++\tfrac{3}{2}S_++\tfrac{3}{2}M_++D_0+\tfrac{1}{2}S_-+\tfrac{1}{2}M_-), \quad (4)$$

$$b_-=(2D_-+\tfrac{3}{2}S_-+\tfrac{3}{2}M_-+D_0+\tfrac{1}{2}S_++\tfrac{1}{2}M_+). \quad (5)$$

To reduce the number of variables, we substitute $2K_+=S_++M_+$ and $2K_-=S_-+M_-$. This substitution fails to simplify the factorials of the denominator. However, we may note that the denominator (and therefore A) is at a minimum when $K_+=M_+=S_+$ and $K_-=M_-=S_-$. At this point, we apply Stirlings approximation for the factorials, transform to molar units and cancel all quantities in W of order $1/N$. Our function after substitution of the constraint

$$d_0=(1-d_+-d_--2k_+-2k_-)$$

becomes

$$\begin{aligned}A=(P)(P+E)\bar{\epsilon}_\alpha+d_0\bar{\epsilon}_0+2(k_++k_-)\bar{\epsilon}_\gamma\\ -RT(1+P)\ln(1+P)+(1-P)\ln(1-P)-d_+\ln d_+\\ -d_-\ln d_--(1-d_+-d_--2k_+-2k_-)\\ \times\ln(1-d_+-d_--2k_+-2k_-)-2k_+\ln k_+\\ -2k_-\ln k_--(d_++d_-+k_++k_-)\ln 4, \quad (6)\end{aligned}$$

where

$$P=(d_+-d_-+k_+-k_-). \quad (7)$$

At this point, we obtain the partial derivatives of A with respect to d_+, d_-, k_+, and k_- and set them equal to zero. Manipulation of these equations leads to the results:

$$k_+=2(d_+{}^3d_-)^{\frac{1}{4}}\exp[-\bar{\epsilon}_\gamma/RT], \quad (8)$$

$$k_-=2(d_+d_-{}^3)^{\frac{1}{4}}\exp[-\bar{\epsilon}_\gamma/RT]. \quad (9)$$

Substitution of these into Eq. (6) reduces the problem to two variables.

Two computer programs were written to study the behavior of this function. The first program plots a grid of the function vs d_+ and d_-. From this grid it is possible to select approximate values of d_+ and d_- for which the minimum occurs. The second program uses the method of steepest descents to locate the minimum exactly. It is also capable of modifying the temperature slightly and relocating the minimum. It is thus possible to easily study the temperature dependence of the function.

ENERGY PARAMETERS

The three energy parameters of the model are constrained to some extent by the experimental data which they are required to fit, but within these limits a small variation in one parameter may be compensated by changes in the other two. The behavior of the model has been investigated on the basis of the following set of parameters which provide a relatively satisfactory fit.

$$KH_2PO_4(KDP_H):\ \bar{\epsilon}_\alpha=-75\ \text{cal/mole}^2,$$
$$\bar{\epsilon}_0=75\ \text{cal/mole},\quad \bar{\epsilon}_\gamma=500\ \text{cal/mole},$$
$$KD_2PO_4(KDP_D):\ \bar{\epsilon}_\alpha=-225\ \text{cal/mole}^2,$$
$$\bar{\epsilon}_0=75\ \text{cal/mole},\quad \bar{\epsilon}_\gamma=500\ \text{cal/mole}.$$

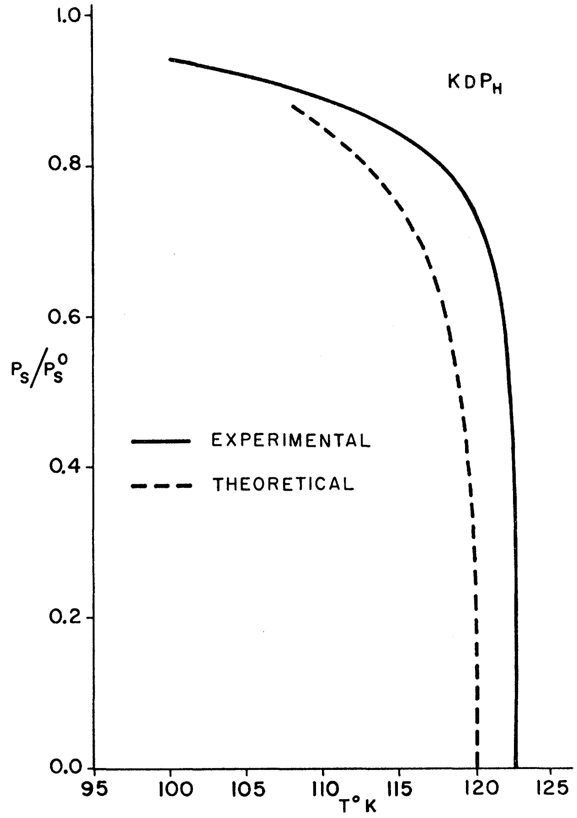

FIG. 3. Spontaneous polarization curves for KDP$_H$. The experimental data are those of A. von Arx and W. Bantle, Helv. Phys. Acta. **16**, 211 (1943).

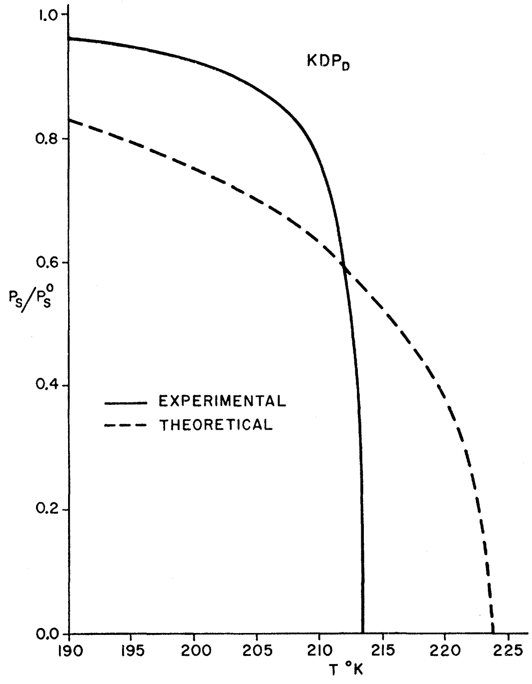

FIG. 4. Spontaneous polarization curves for KDP$_D$. The experimental data are those of Zwicker and Scherrer (see footnote 3).

The only difference in energy parameters between KDP$_H$ and KDP$_D$ is the change in $\bar{\epsilon}_\alpha$. This is based on the observed change in maximum spontaneous polarization.[3] The other energy parameters may be expected to vary to some extent, but they were held constant in the present calculations.

RESULTS OF CALCULATIONS

The calculated and experimental spontaneous polarization curves are presented in Figs. 3 and 4. On the basis of the arbitrary constraint imposed on $\bar{\epsilon}_0$ and $\bar{\epsilon}_\gamma$ one, but not both, of the curves can be made to agree very closely with the experimental data. There is, however, some basis for assuming that $\bar{\epsilon}_\gamma$ is larger in KDP$_D$. The addition of a deuterium to the positive end of the larger dipole should be more energetically unfavorable. This correction would sharpen the spontaneous polarization curve for KDP$_D$.

The calculated dielectric constant ϵ_c for KDP$_H$ is shown in Fig. 5. This was obtained from the numerical relation

$$\epsilon_c=4\pi\Delta P/\Delta E.$$

The calculated dielectric constant has a number of interesting features. First of all, it reproduces the sharp maximum found experimentally. The low-field dielectric constant obeys the Curie law with a Curie constant of about 850°K; this is about one-fourth the experimental value for the free crystal. It is possible to calculate the field dependence, and above the Curie point it is, at least qualitatively, reproduced. Baum-

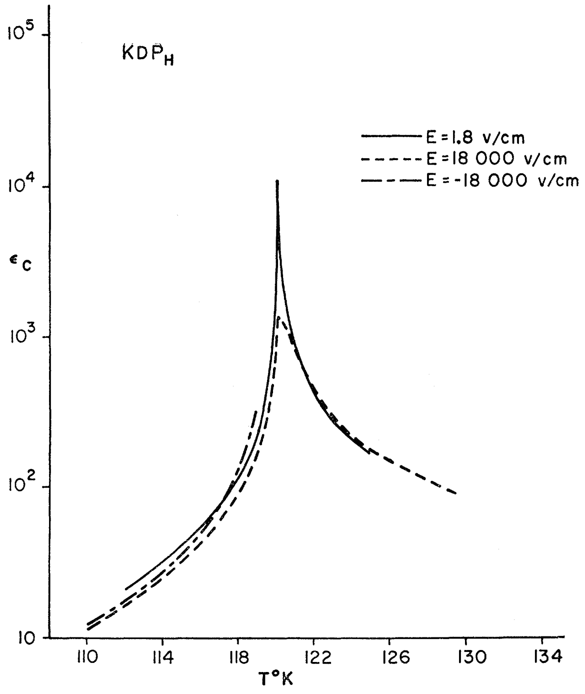

FIG. 5. Calculated dielectric constant of KDP$_H$ for various values of applied field.

gartner's data[14] implies a crossing of the dielectric constants measured with different fields. This crossing in his data occurs about four degrees above the transition; in our plot it occurs about two degrees above the transition. Figure 6 gives a comparison with experimental data; ϵ_c drops off rapidly below the Curie point; this is in much better agreement with the data of Barkla and Finlayson[4] than the ϵ_c which they derived from Mason's theory. Finally, the peak height is indeed lowered by an increase in measuring field. The transition heat for KDP$_H$ from 110°K to 125°K is 132 cal/mole. The model above the transition point has a constant heat capacity of about 1 cal/mole-degree which cannot be separated from the normal heat capacity. With this correction our entropy of transition is approximately 1 cal/mole-degree. This is still significantly larger than the 0.72 cal/mole-degree measured by Stevenson and Hooley.[1]

ANTIFERROELECTRIC BEHAVIOR

Since ammonium dihydrogen phosphate has essentially the same crystal structure, we would expect the model to also reproduce some of the characteristics of antiferroelectric behavior. Figure 7 shows the behavior of a dielectric constant calculated with the following parameters:

$$\bar{\epsilon}_\alpha = -75 \text{ cal/mole}^2, \quad \bar{\epsilon}_0 = -220 \text{ cal/mole},$$
$$\bar{\epsilon}_\gamma = 500 \text{ cal/mole}.$$

If $\bar{\epsilon}_0$ is more negative than $\bar{\epsilon}_\alpha$, the model exhibits no spontaneous polarization. In addition, the dielectric constant shows a Curie law dependence with a negative Curie temperature as has been found by Nagamiya.[7] In this instance, it appears that our microscopic model parallels the model of Nagamiya which uses a combination of macroscopic and microscopic quantities. Both models require a negative $\bar{\epsilon}_0$; this implies that the ammonium ion acts to stabilize the D_0 configurations. The model does not, at present, explain the first-order transition found in ADP. Mason has suggested that this transition may be due to disordering of the ammonium ions and, therefore, not be directly connected with the ferroelectric properties.[15]

DISCUSSION

The ferroelectric effect in the dihydrogen phosphates can be characterized by the measurement of a number of properties, for example, spontaneous polarization, dielectric constant, electric field dependent behavior, infrared absorption, transition heat, switching time, coercive force, etc. It may also be characterized by the effect of chemical substitution, primarily that of deuterium for hydrogen, on the above properties. The construction of a model theory is primarily a search for the important energies of interaction and an adequate description of the mechanism of interactions. An ideal theory should, within the framework of its assumptions, then provide results which are in agreement or, at least, not inconsistent with all the experimental facts.

At the present time, no one model can describe all the experimental facts in an adequate fashion; but perhaps consideration of both long- and short-range forces is a

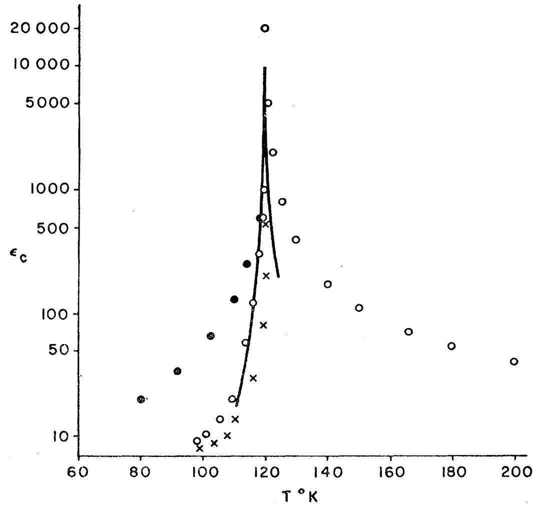

FIG. 6. Comparison of calculated dielectric constant (solid line) with previous work. (See footnote 4.) Mason's theory ●; Mueller's theory ✕; Barkla and Finlayson's experimental data ○.

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[14] H. Baumgartner, Helv. Phys. Acta. **23**, 651 (1950).

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closer approach to an ideal theory in that it presents a more complete discussion of the effect than previous theories. This point may be made more clear by considering the various properties.

Spontaneous Polarization

Previously, Takagi[12] had given the most satisfactory description of the temperature dependence of this property with its rather sharp knee at the transition point. Pirenne[10] has suggested that his spontaneous polarization curves may be brought into agreement by consideration of a P^4 term which arises from elastic deformation of the hydrogen bond. However, it appears from diffraction measurements that there is not a direct relation between these quantities. The bond length first increases then decreases with increasing polarization.[5,16] Since the macroscopic elastic energies seem to be too small to explain the observed effect,[10] the most satisfactory explanation appears to lie in the consideration of near-neighbor interactions as presented by Takagi and the present model.

Pirenne[9] has advanced the only quantitative explanation of the increase in saturation polarization due to deuteration of the compound. This explanation is, however, based on the presence of new low-lying levels in the hydrogen bond. Further investigation is desirable for understanding these levels and the motions which are related to them. An alternative qualitative explanation might be sought in the increased covalency of the shorter proton bond. In this bond-length range, it appears that covalent contributions to the bond become increasingly important and a small change in bond length may result in a quite different ionic character for the bond and therefore a much different dipole moment in the phosphate tetrahedron. Deuterium substitution also results in a relatively sharper knee in the spontaneous polarization curve. This may be obtained in our model by the discussed increase in $\bar{\epsilon}_\gamma$. A further investigation is necessary to determine whether this change can be justified.

The only other complete discussion of the temperature dependence of the dielectric constant is that of Mason.[8] Our model appears to provide a more satisfactory qualitative description of the low-temperature dependence found by Barkla and Finlayson[4] although Mason's theory provides a more quantitative description of the high-temperature behavior. Neither theory agrees with the low-temperature ϵ_c behavior found by Busch[17]; this may be due to domain wall motion in his measurements.

The field dependence of the dielectric constant appears to have been previously discussed only by Baumgartner[14] using empirical functions. The field dependence in our model arises in a simple fashion from the preliminary assumptions about the free-energy function and again appears to have the correct qualitative behavior.

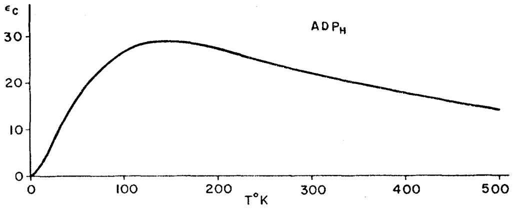

FIG. 7. Calculated dielectric constant of ADP.

Infrared results seem to indicate that the KDP hydrogen bond in most respects is similar to hydrogen bonds in nonferroelectric materials and does not change drastically during the ferroelectric transition. Both stretching and in-plane bending motions have been assigned to bands lying above 1000 cm^{-1}.[18] It would appear that neither of these motions is available for use in the Pirenne model. At the transition our model would predict no great change in the infrared spectra. We might expect hydrogen attached to M and S configurations to display slightly different behavior, but the total concentration of these species does not exceed 15%, and this absorption could be easily lost under the extremely broad bands of the D_+, D_-, and D_0 configurations. At the present time, any further knowledge of the behavior of the hydrogen bonds in this material would be extremely useful, since their properties determine a number of the fundamental energies of interaction.

Heat of Transition

The most satisfactory value for this quantity has been given by Takagi although the values of Slater, Pirenne, and the present theory are in fair agreement considering the necessary model assumptions.

In the realm of other properties, it appears that only Mason has given an explanation of the low coercive field.

CONCLUSIONS

Since our model appears to provide an adequate representation of a large number of the ferroelectric properties of the dihydrogen phosphates, it may perhaps be useful to note some conclusions which can be based upon it. First, one may conclude from antiferroelectric behavior of ADP and the shift in Curie temperature due to deuteration that both near-neighbor and long-range forces play significant parts on the ferroelectric effect. Second, again from the behavior of ADP, one can suggest that in some instances it is necessary to consider the interactions between energy levels which arise from what are normally termed ferroelectric and antiferro-

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electric arrangements of the crystal, since entropy may be gained from populating both types of levels. Although these suggestions are based on a model for the dihydrogen phosphates, it appears that they may also be important in the construction of model theories for other ferroelectric materials.

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Elastic Constants of Ammonium Dihydrogen Phosphate (ADP) and the Laval Theory of Crystal Elasticity*

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The acoustic shear wave velocities v_{yz} and v_{zy} have been measured in ADP by the direct method of piezoelectric resonances, and by the direct pulse-echo method. These velocities are found with each method to be equal within the experimental uncertainty. The resonance results have a probable error of 0.1% for the difference between the corresponding Laval elastic constants c_{44} and c_{77}. This experimental result disagrees with those previously obtained with ADP by indirect methods.

INTRODUCTION

IN the established theory of crystal elasticity, the state of strain in a volume element is described by a symmetrical tensor. In terms of an orthogonal coordinate system there are three shear strain components[1]:

$$S_4=\partial u_y/\partial z+\partial u_z/\partial y;\quad S_5=\partial u_z/\partial x+\partial u_x/\partial z;\quad S_6=\partial u_x/\partial y+\partial u_y/\partial x.\qquad (1)$$

These strain components measure the change in angle between the vectors in the strained crystal medium which are parallel to the coordinate axes in the unstrained condition. The strain components are unaffected by a rotation of the volume element.

About ten years ago, J. Laval proposed a modified theory of crystal elasticity in which the strain and stress tensors may be unsymmetrical. This theory has been expounded in detail by LeCorre.[2,3] As a consequence, the number of independent elastic constants would be increased. For instance, LeCorre replaces the elastic shear constant c_{44} by two different constants c_{44} and c_{77} whenever the Y and Z directions in a crystal are not equivalent. This would make the elastic energy dependent on rotation. One would hesitate to consider this theory seriously for static deformation, but there is some intuitive appeal in the concept that wave propagation in the Z direction with particle motion in the Y direction may be controlled by a different elastic constant from that involved in wave propagation parallel to Y and particle motion parallel to Z. The present authors have not found a theoretical foundation for this intuitive assumption as long as the elastic wavelength remains large compared to the lattice constants, and electric boundary conditions are taken into account for piezoelectric crystals. Nevertheless, some experimental work seemed called for in view of the serious consideration given the Laval theory[4–6] and the impact that its verification would have on the whole body of elastic constant measurements.

Experimental confirmation of deviation from classical elastic theory has rested largely on observation of light diffraction by ultrasonic waves in ammonium dihydrogen phosphate (ADP) which belongs to crystal class $V_d=\bar{4}2m$. For this crystal, LeCorre[2] claimed a value of 1.36 ± 0.11 for the ratio c_{44}/c_{77}, while Joel and

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[*] The work done at the Case Institute of Technology was supported by the U. S. Atomic Energy Commission.

[1] For the nomenclature here used, see Institute of Radio Engineers, New York: Standards on Piezoelectric Crystals, 1949.

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