

Properties of a Tetragonal Antiferroelectric Crystal

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In order to interpret the properties of the tetragonal crystal $\text{ND}_4\text{D}_2\text{PO}_4$ (deuterated ADP) a thermodynamic treatment has been developed which relates the observed crystal structure change and the dielectric constant change at the transition temperature to the appearance of spontaneous polarization. For an antiferroelectric crystal, the average spontaneous polarization is zero, being oppositely directed for adjacent layers, but the square of the spontaneous polarization is large. This results in quadratic strain components which cause a change in the crystal structure below the transition temperature. It is shown that the change observed is consistent with an antiferroelectric arrangement with one of the a axes being the antiferroelectric axis. The dielectric constants in all three directions suffer a large drop below the transition temperature.

IN order to evaluate the possible mechanical distortions, the relations between the dielectric constants and the changes in specific heat capacities to be expected in the tetragonal crystal $\text{ND}_4\text{D}_2\text{PO}_4$ ¹ that becomes antiferroelectric below a definite transition temperature Θ_0 , a phenomenological development of the strains, electric fields, and entropy has been made in terms of the independent variables stresses, electric displacements, and temperature Θ . Since as the temperature decreases through the transition temperature Θ_0 , the measured changes are strains, remanent polarizations, and entropy changes, this type of formulation is the most useful one for discussing the transition. This requires the use of one of the Gibb's potentials G_1 , given in terms of the internal energy function U , by

$$G_1 = U - S_{ij}T_{ij} - \sigma\Theta, \quad (1)$$

where S_{ij} are the strains expressed in tensor form, T_{ij} the stresses, σ the entropy, and Θ the temperature. In rationalized mks units the differential form is

$$dG_1 = -S_{ij}dT_{ij} + E_m dD_m - \sigma d\Theta, \quad (2)$$

TABLE I. First-order derivatives of the potential G_1 and their physical significance.

Derivative	Relationship between derivatives	Symbol	Name
$\frac{\partial S_{ij}}{\partial T_{kl}}$		$s_{ijkl}^{D, \Theta}$	Elastic compliances at constant displacement and temperature
$\frac{\partial S_{ij}}{\partial D_n}$	$= \frac{-\partial^2 G_1}{\partial T_{ij} \partial D_n} = \frac{-\partial E_m}{\partial T_{ij}}$	g_{ijn}	Piezoelectric constants
$\frac{\partial S_{ij}}{\partial \Theta}$	$= \frac{-\partial^2 G_1}{\partial T_{ij} \partial \Theta} = \frac{\partial \sigma}{\partial T_{ij}}$	α_{ij}	Temperature expansion coefficients
$\frac{\partial E_m}{\partial D_n}$		β_{mn}	Dielectric impermeability coefficients
$\frac{\partial E_m}{\partial \Theta}$	$= \frac{\partial G_1}{\partial D_n \partial \Theta} = -\frac{\partial \sigma}{\partial D_n}$	q_m	Pyroelectric constants
$\frac{\partial \sigma}{\partial \Theta}$		$\frac{\rho C^T D}{\Theta}$	Density times specific heat per unit mass at constant stress and electric displacement divided by the absolute temperature Θ

¹ The data for $\text{ND}_4\text{D}_2\text{PO}_4$ are given by W. P. Mason and B. T. Matthias, preceding paper [Phys. Rev. 88, 477 (1952)].

and hence,

$$S_{ij} = -\partial G_1 / \partial T_{ij}; \quad E_m = \partial G_1 / \partial D_m; \quad \sigma = -\partial G_1 / \partial \Theta, \quad (3)$$

where E_m and D_m are, respectively, the electric fields and the electric displacement components.

Developing the strains, electric fields, and entropy in a Maclaurin series about the points of zero stresses, zero displacements, and temperature Θ_0 , we have up to second derivatives of the stresses and temperatures, but higher derivatives of the electric displacements:

$$S_{ij} = \frac{\partial S_{ij}}{\partial T_{kl}} T_{kl} + \frac{\partial S_{ij}}{\partial D_n} D_n + \frac{\partial S_{ij}}{\partial \Theta} (\Theta - \Theta_0) + \frac{1}{2!} \left[\frac{\partial^2 S_{ij}}{\partial T_{kl} \partial T_{qr}} T_{kl} T_{qr} + \frac{2\partial^2 S_{ij}}{\partial T_{kl} \partial D_n} T_{kl} D_n + 2 \frac{\partial^2 S_{ij}}{\partial T_{kl} \partial \Theta} T_{kl} (\Theta - \Theta_0) + \frac{\partial^2 S_{ij}}{\partial D_n \partial D_o} D_n D_o + \frac{2\partial^2 S_{ij}}{\partial D_n \partial \Theta} D_n (\Theta - \Theta_0) + \frac{\partial^2 S_{ij}}{\partial \Theta^2} (\Theta - \Theta_0)^2 \right] + \frac{1}{3!} \frac{\partial^3 S_{ij}}{\partial D_n \partial D_o \partial D_p} D_n D_o D_p + \dots, \quad (4)$$

$$E_m = \frac{\partial E_m}{\partial T_{kl}} T_{kl} + \frac{\partial E_m}{\partial D_n} D_n + \frac{\partial E_m}{\partial \Theta} (\Theta - \Theta_0) + \frac{1}{2!} \left[\frac{\partial^2 E_m}{\partial T_{kl} \partial T_{qr}} T_{kl} T_{qr} + 2 \frac{\partial^2 E_m}{\partial T_{kl} \partial D_n} T_{kl} D_n + \frac{2\partial^2 E_m}{\partial T_{kl} \partial \Theta} T_{kl} (\Theta - \Theta_0) + \frac{\partial^2 E_m}{\partial D_n \partial D_o} D_n D_o + \frac{2\partial^2 E_m}{\partial D_n \partial \Theta} D_n (\Theta - \Theta_0) + \frac{\partial^2 E_m}{\partial \Theta^2} (\Theta - \Theta_0)^2 \right] + \frac{1}{3!} \frac{\partial^3 E_m}{\partial D_n \partial D_o \partial D_p} D_n D_o D_p + \frac{1}{4!} \frac{\partial^4 E_m}{\partial D_n \partial D_o \partial D_p \partial D_s} D_n D_o D_p D_s + \frac{1}{5!} \frac{\partial^5 E_m}{\partial D_n \partial D_o \partial D_p \partial D_s \partial D_t} D_n D_o D_p D_s D_t + \dots,$$

TABLE II. Second-order derivatives of the potential G_1 and their physical significance.

Derivative	Relationship between derivatives	Symbol	Name
$\frac{\partial^2 S_{ij}}{\partial T_{kl} \partial T_{qr}}$	— assumed zero		Change of elastic compliances with stress
$\frac{\partial^2 S_{ij}}{\partial T_{kl} \partial D_n} = -\frac{\partial^3 G_1}{\partial T_{ij} \partial T_{kl} \partial D_n} = -\frac{\partial^2 E_m}{\partial T_{kl} \partial T_{qr}}$	neglected		Change of elastic compliance with electric displacement
$\frac{\partial^2 S_{ij}}{\partial T_{kl} \partial \Theta} = -\frac{\partial^3 G_1}{\partial T_{ij} \partial T_{kl} \partial \Theta} = -\frac{\partial^2 E_n}{\partial T_{ij} \partial T_{kl}}$	T^{sijkl}		Rate of change of the elastic compliances with temperature
$\frac{\partial^2 S_{ij}}{\partial D_n \partial D_o} = -\frac{\partial^3 G_1}{\partial T_{ij} \partial D_n \partial D_o} = -\frac{\partial^2 E_n}{\partial T_{ij} \partial D_o}$	Q_{ijn}		Quadratic strain components
$\frac{\partial^2 S_{ij}}{\partial D_n \partial \Theta} = -\frac{\partial^3 G_1}{\partial T_{ij} \partial D_n \partial \Theta} = -\frac{\partial^2 E_n}{\partial T_{ij} \partial \Theta} = -\frac{\partial^2 \sigma}{\partial T_{ij} \partial D_n}$	T_{\thetaijn}		Rate of change of piezoelectric constants with temperature
$\frac{\partial^2 S_{ij}}{\partial \Theta^2} = -\frac{\partial^3 G_1}{\partial T_{ij} \partial \Theta^2} = \frac{\partial^2 \sigma}{\partial T_{ij} \partial \Theta}$	$T_{\alpha ij}$		Rate of change of temperature expansion coefficients with temperature
$\frac{\partial^2 E_m}{\partial D_n \partial \Theta} = \frac{\partial^3 G_1}{\partial D_n \partial D_n \partial \Theta} = -\frac{\partial^2 \sigma}{\partial D_n \partial D_n}$	$T_{\beta mn}$		Rate of change of dielectric impermeability with temperature
$\frac{\partial^2 E_m}{\partial \Theta^2} = \frac{\partial^3 G_1}{\partial D_n \partial \Theta^2} = -\frac{\partial^2 \sigma}{\partial D_n \partial \Theta}$	T_{qmn}		Rate of change of pyroelectric constants with temperature
$\frac{\partial^2 \sigma}{\partial \Theta^2}$	$\frac{\partial}{\partial \Theta} \left(\frac{\rho C^T}{\Theta_0} \right)$		Rate of change of temperature derivative of entropy with temperature

$$\begin{aligned}
(\sigma - \sigma_0) &= \frac{\partial \sigma}{\partial T_{kl}} T_{kl} + \frac{\partial \sigma}{\partial D_n} D_n + \frac{\partial \sigma}{\partial \Theta} (\Theta - \Theta_0) \\
&+ \frac{1}{2!} \left[\frac{\partial^2 \sigma}{\partial T_{kl} \partial T_{qr}} T_{kl} T_{qr} + \frac{2 \partial^2 \sigma}{\partial T_{kl} \partial D_n} T_{kl} D_n \right. \\
&+ \frac{2 \partial^2 \sigma}{\partial T_{kl} \partial \Theta} T_{kl} (\Theta - \Theta_0) + \frac{\partial^2 \sigma}{\partial D_n \partial D_o} D_n D_o \\
&\left. + \frac{2 \partial^2 \sigma}{\partial D_n \partial \Theta} D_n (\Theta - \Theta_0) + \frac{\partial^2 \sigma}{\partial \Theta^2} (\Theta - \Theta_0)^2 \right] \\
&+ \frac{1}{3!} \frac{\partial^3 \sigma}{\partial D_n \partial D_o \partial D_p} D_n D_o D_p + \dots
\end{aligned}$$

In the differentiations, the conditions for partial differentiation are not written but are understood; for example,

$$\partial S_{ij} / \partial T_{kl} = (\partial S_{ij} / \partial T_{kl})_{D, \Theta}, \quad (5)$$

i.e., the electric field and the temperature are held constant during the differentiation.

In these equations there are some equivalences between the partial derivatives because of the fact that the order of differentiation can be inverted. For example,

$$\partial S_{ij} / \partial D_n = -\partial^2 G_1 / \partial T_{ij} \partial D_n = -\partial E_m / \partial T_{ij} = g_{ijn}, \quad (6)$$

a piezoelectric constant relating the strain and the electric displacement. Table I shows all the first-order derivatives, their relationships, the symbols given them, and their names.

Similar relationships and names for the second derivatives are shown by Table II.

All second derivatives involving two differentiations by stresses are neglected as being very small. Also neglected is the change in elastic compliance constants with electric displacement since no measurements have been made of this effect.

The higher derivatives of interest are third, fourth, fifth, and sixth rank tensors representing the additions to the G_1 function due to third, fourth, fifth, and sixth power products of the dielectric displacements. These have been given the designations

$$\begin{aligned}
\frac{\partial^2 E_m}{\partial D_n \partial D_o} &= K_{mno}, & \frac{\partial^3 E_m}{\partial D_n \partial D_o \partial D_p} &= K_{mnop}, \\
\frac{\partial^4 E_m}{\partial D_n \partial D_o \partial D_p \partial D_s} &= K_{mnopst}, & \frac{\partial^5 E_m}{\partial D_n \partial D_o \partial D_p \partial D_s \partial D_t} &= K_{mnopst}. \quad (7)
\end{aligned}$$

With these symbols, the three equations representing the strains, fields, and the entropy can be written in

the forms

$$S_{ij} = [s_{ijkl} D_n^\Theta + T_{sijkl}(\Theta - \Theta_0)] T_{kl} + [g_{ijn} + T_{gijn} \times (\Theta - \Theta_0)] D_n + (\alpha_{ij} + \frac{1}{2} T_{\alpha_{ij}}(\Theta - \Theta_0))(\Theta - \Theta_0) + \frac{1}{2} Q_{ijno} D_n D_o + \dots, \quad (8)$$

$$E_m = -[g_{mkl} + T_{g_{mkl}}(\Theta - \Theta_0)] T_{kl} + [\beta_{mn} + T_{\beta_{mn}} \times (\Theta - \Theta_0)] D_n + \left[q_m + \frac{T_{q_m}(\Theta - \Theta_0)}{2} \right] [\Theta - \Theta_0] - Q_{mnkl} T_{kl} D_n + \frac{K_{mno} D_n D_o}{2} + \frac{K_{mnop}}{3!} D_n D_o D_p - \frac{K_{mnopst}}{4!} D_n D_o D_p D_s + \frac{K_{mnopst}}{5!} D_n D_o D_p D_s D_t + \dots$$

$$(\sigma - \sigma_0) = (\alpha_{ij} + T_{\alpha_{ij}}(\Theta - \Theta_0)) T_{kl} - (q_m + T_{q_m}(\Theta - \Theta_0)) D_m + \left[\frac{\rho C^{T,\Theta}}{\Theta_0} + \frac{1}{2} \frac{\partial}{\partial \Theta} \left(\frac{\rho C^{T,\Theta}}{\Theta_0} \right) \times (\Theta - \Theta_0) \right] (\Theta - \Theta_0) + \frac{1}{2!} [T_{sijkl} T_{kl} T_{qr} + 2T_{\theta_{kl}} T_{kl} D_n - T_{\beta_{mn}} D_n D_o].$$

Hence, as the temperature increases from below the transition temperature where D_n and D_o are positive to above the transition temperature where $D_n = D_o = 0$, an increase in entropy (i.e., a decrease in order) takes place as long as $T_{\beta_{mn}}$ is positive.

These equations can all be derived from a potential G_1 given by

$$G_1 = -\frac{1}{2} [s_{ijkl} D_n^\Theta + T_{sijkl}(\Theta - \Theta_0)] T_{ij} T_{kl} - [g_{ijn} + T_{g_{ijn}}(\Theta - \Theta_0)] T_{ij} D_n + \frac{1}{2} [\beta_{mn} + T_{\beta_{mn}}(\Theta - \Theta_0)] D_m D_n - \left[\alpha_{ij} + \frac{T_{\alpha_{ij}}(\Theta - \Theta_0)}{2} \right] \times T_{ij}(\Theta - \Theta_0) + \left[q_m + \frac{T_{q_m}(\Theta - \Theta_0)}{2} \right] D_m(\Theta - \Theta_0) - \frac{1}{2} Q_{ijno} D_n D_o T_{ij} + \frac{K_{mno}}{3!} D_m D_n D_o + \frac{K_{mnop}}{4!} \times D_m D_n D_o D_p + \frac{K_{mnopst}}{5!} D_m D_n D_o D_p D_s + \frac{K_{mnopst}}{6!} \times D_m D_n D_o D_p D_s D_t + \left[\frac{\rho C^{T,\Theta}}{\Theta_0} + \frac{1}{2} \frac{\partial}{\partial \Theta} \left(\frac{\rho C^{T,\Theta}}{\Theta_0} \right) \times (\Theta - \Theta_0) \right] [\Theta - \Theta_0]. \quad (9)$$

Applying the differentiations of Eqs. (3) to this function, the equations of (8) result.

For tetragonal symmetry $D_{2d}(\bar{4}2m)$ it is well known that the tensors up to the fourth rank have the matrices

$$q_m = 0; \alpha_{ij}; \beta_{mn}; \begin{vmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{11} & 0 \\ 0 & 0 & \alpha_{33} \end{vmatrix};$$

$$g_{ijm} = \begin{vmatrix} 0 & 0 & 0 & g_{123} & 0 & 0 \\ 0 & 0 & 0 & 0 & g_{123} & 0 \\ 0 & 0 & 0 & 0 & 0 & g_{312} \end{vmatrix};$$

$$K_{mno} = \begin{vmatrix} 0 & 0 & 0 & K_{123} & 0 & 0 \\ 0 & 0 & 0 & 0 & K_{123} & 0 \\ 0 & 0 & 0 & 0 & 0 & K_{123} \end{vmatrix};$$

$$s_{ijkl} = \begin{vmatrix} s_{1111} & s_{1122} & s_{1133} & 0 & 0 & 0 \\ s_{1122} & s_{1111} & s_{1133} & 0 & 0 & 0 \\ s_{1133} & s_{1133} & s_{3333} & 0 & 0 & 0 \\ 0 & 0 & 0 & s_{2323} & 0 & 0 \\ 0 & 0 & 0 & 0 & s_{2323} & 0 \\ 0 & 0 & 0 & 0 & 0 & s_{1212} \end{vmatrix};$$

$$Q_{ijno} = \begin{vmatrix} Q_{1111} & Q_{1122} & Q_{1133} & 0 & 0 & 0 \\ Q_{1122} & Q_{1111} & Q_{1133} & 0 & 0 & 0 \\ Q_{3311} & Q_{3311} & Q_{3333} & 0 & 0 & 0 \\ 0 & 0 & 0 & Q_{2323} & 0 & 0 \\ 0 & 0 & 0 & 0 & Q_{2323} & 0 \\ 0 & 0 & 0 & 0 & 0 & Q_{1212} \end{vmatrix};$$

$$K_{mnop} = \begin{vmatrix} K_{1111} & K_{1122} & K_{1133} & 0 & 0 & 0 \\ K_{1122} & K_{1111} & K_{1133} & 0 & 0 & 0 \\ K_{1133} & K_{1133} & K_{3333} & 0 & 0 & 0 \\ 0 & 0 & 0 & K_{1133} & 0 & 0 \\ 0 & 0 & 0 & 0 & K_{1133} & 0 \\ 0 & 0 & 0 & 0 & 0 & K_{1122} \end{vmatrix}. \quad (10)$$

The fifth rank tensor K_{mnopst} for the symmetry $(\bar{4}2m)$ can be determined by applying the two conditions

$$z = -z; x = y; y = x; x = x; y = -y; z = -z \quad (11)$$

and the equation of tensor transformation

$$K'_{mnopst} = \frac{\partial x'_m}{\partial x_m} \frac{\partial x'_n}{\partial x_n} \frac{\partial x'_o}{\partial x_o} \frac{\partial x'_p}{\partial x_p} \frac{\partial x'_s}{\partial x_s} K_{mnopst}.$$

The results of applying these two conditions to the tensor K_{mnopst} is that all terms are zero except

$$K_{11123} = K_{12223} \quad \text{and} \quad K_{12333}, \quad (12)$$

with all permutations of these terms being equal since all of the D components can be interchanged. Hence, fifth rank terms enter only if polarization exists along all three axes.

For the sixth rank tensor the nonvanishing components when all the subscripts can be interchanged are

for the two conditions

$$\begin{aligned} K_{111111} &= K_{222222}; K_{111122} = K_{112222}; K_{111133} = K_{222233}, \\ K_{113333} &= K_{223333}; K_{112233}; K_{333333}; \end{aligned} \quad (13)$$

and hence the energy terms added by the sixth rank tensor are

$$\begin{aligned} &K^*_{111111}[D_1^6 + D_2^6] + K^*_{333333}D_3^6 + K^*_{111122} \\ &\times [D_1^4D_2^2 + D_2^4D_1^2] + K^*_{111133}[D_1^4D_3^2 + D_2^4D_3^2] \\ &+ K^*_{112233}D_1^2D_2^2D_3^2 + K^*_{113333}[D_1^2D_3^4 + D_2^2D_3^4], \end{aligned} \quad (14)$$

where the stars indicate that the term is multiplied by the number of different combinations that can be obtained by interchanging the subscripts and dividing by 6!

One fact that is obvious from the form of the quadratic strain constants Q_{ijno} is that if the spontaneous polarization were along the z or 3 direction, the change along x given by Q_{1133} has to equal the change along y given by $Q_{2233} = Q_{1133}$, and hence the crystal will still be tetragonal. On the other hand, if the polarization lies along either x or y , the changes introduced by the quadratic effects are different for all three axes and hence the crystal can change from tetragonal to orthorhombic as observed experimentally. We can rule out the possibility that antiferroelectric polarization occurs simultaneously along both x and z by the fact that no shear displacements of the type generated by terms of the form Q_{2323} are observed.

If all the stresses are zero and we consider only the electric displacements, all the energy terms are represented by the β and K terms. To determine the dielectric constants for small fields we need consider only large spontaneous terms along x and small electric displacements in addition along x , y , and z . We neglect all products of small terms above the second, and hence the only remaining terms are

$$\begin{aligned} G_1 &= \frac{1}{2}[\beta_{11} + T\beta_{11}(\Theta - \Theta_0)][(D_{1c} + \Delta D_1)^2 + D_2^2] \\ &+ [\beta_{33} + T\beta_{33}(\Theta - \Theta_0)]D_3^2 + K^*_{1111}[(D_{1c} + \Delta D_1)^4] \\ &+ K^*_{1122}[D_{1c}^2D_2^2] + K^*_{1133}[D_{1c}^2D_3^2] + K^*_{111111} \\ &\times [D_{1c} + \Delta D_1]^6 + K^*_{111122}[D_{1c}^4D_2^2] \\ &+ K^*_{111133}D_3^2D_{1c}^4 + G_0. \end{aligned} \quad (15)$$

In a manner similar to that discussed by Kittel,² the polarization along the antiferroelectric axis can be calculated by requiring that the value of G_1 shall be the same below and above the transition temperature and that the first derivative of G_1 by D_1 —which equals the field—shall also be zero. This results in two equations:

$$\beta_{11} + 2K^*_{1111}D_{1c}^2 + 2K^*_{111111}D_{1c}^4 = 0, \quad (16)$$

$$\beta_{11} + 4K^*_{1111}D_{1c}^2 + 6K^*_{111111}D_{1c}^4 = 0. \quad (17)$$

Solving these equations simultaneously, we find

$$D_{1c}^2 = -\beta_{11}/K^*_{1111}; \quad K^*_{111111} = K^*_{1111}^2/2\beta_{11}. \quad (18)$$

² C. Kittel, Phys. Rev. **82**, 729 (1951).

For any temperature, since Eq. (17) is valid, we find

$$\begin{aligned} D_1^2 &= -\frac{2\beta_{11}}{3K^*_{1111}} - \frac{2\beta_{11}}{3K^*_{1111}} \\ &= \frac{2}{3}D_{1c}^2 + \frac{2}{3}D_{1c}^2 \left[1 - \frac{3}{4} \left(1 + \frac{T\beta_{11}(\Theta - \Theta_0)}{\beta_{11}} \right) \right]^{\frac{1}{2}}. \end{aligned} \quad (19)$$

Hence the spontaneous polarization increases below the transition point.

The dielectric constant along the x axis for small applied fields is given by

$$\begin{aligned} \Delta E_1 &= [\beta_{11} + T\beta_{11}(\Theta - \Theta_0)][D_{10} + \Delta D_1] \\ &+ 4K^*_{1111}[D_{10}^3 + 3D_{10}^2\Delta D_1] \\ &+ 6K^*_{111111}[D_{10}^5 + 5D_{10}^4\Delta D_1]. \end{aligned} \quad (20)$$

Since

$$[\beta_{11} + T\beta_{11}(\Theta - \Theta_0)]D_{10} + 4K^*_{1111}D_{10}^3 + 6K^*_{111111}D_{10}^5$$

is zero for all temperatures, then

$$\Delta D_1/\Delta E_1 = \epsilon = \{[\beta_{11} + T\beta_{11}(\Theta - \Theta_0)] + 12K^*_{1111}D_{10}^2 + 30K^*_{111111}D_{10}^4\}^{-1}. \quad (21)$$

Just above the Curie temperature Θ_0 ,

$$D_{10} = 0 \quad \text{and} \quad \epsilon_{11}^+ = 1/\beta_{11}. \quad (22)$$

Just below, introducing the values of D_{1c}^2 and K^*_{111111} from (18),

$$\epsilon_{11}^- = 1/4\beta_{11}, \quad (23)$$

and the dielectric constant drops to $\frac{1}{4}$ the value just above the Curie temperature. This is a somewhat arbitrary result which depends on the sixth power term furnishing the potential to limit the increase in polarization. If this term varies as the n th power of D_1 it is readily shown that the dielectric constant below the transition drops to $1/(n-2)$. For $\text{ND}_4\text{D}_2\text{PO}_4$ the ratio along an a axis is about 8 to 1.

The dielectric constants along the y and z axes (i.e., the two nonantiferroelectric axes) can be calculated in a similar manner and are

$$\begin{aligned} \epsilon_{22} &= \{[\beta_{11} + T\beta_{11}(\Theta - \Theta_0)] + 2K^*_{1122}D_{10}^2 \\ &+ 2K^*_{111122}D_{10}^4\}^{-1}; \\ \epsilon_{33} &= \{[\beta_{33} + T\beta_{33}(\Theta - \Theta_0)] + 2K^*_{1133}D_{10}^2 \\ &+ K^*_{111133}D_{10}^4\}^{-1}. \end{aligned} \quad (24)$$

Hence the dielectric constants along y and z will also drop below the transition temperature by amounts depending on the values of the K constants. Along z the drop is about 4 to 1.

An approximate value of the spontaneous polarization of $\text{ND}_4\text{D}_2\text{PO}_4$ can be obtained from the heat of

transition measurements¹ ΔH of Stephenson and Zettlemoyer³ and the temperature coefficient of the dielectric impermeability constant along the x axis determined from the dielectric measurements of Fig. 2 of the companion paper.¹ The heat of transition ΔH has been found to be $\Delta H = 154 \pm 5$ calories per mole for normal ammonium dihydrogen phosphate. From Eq. (8), the decrease in entropy due to ordering is in cgs units

$$\Delta\sigma = (4\pi/2)T_{\beta_{11}}P_1^2, \quad (25)$$

where P_1 is the polarization per square centimeter.

³ C. C. Stephenson and A. C. Zettlemoyer, *J. Am. Chem. Soc.* **66**, 1405 (1944).

The heat of transition in calories per mole is equal to

$$\Delta H = \frac{\Theta_0 \Delta\sigma M}{4.187 \times 10^7 \rho} = \frac{2\pi T_{\beta_{11}} \Theta_0 P_1^2 M}{4.187 \times 10^7 \rho}, \quad (26)$$

where M is the molecular weight and ρ the density. From Fig. 2 of reference 1, $T_{\beta_{11}} = 0.000065$, $M = 115.08$, $\rho = 1.804$, and since $\Delta H = 154$ calories per mole the indicated spontaneous polarization per unit area is

$$P_1 = 32,000 \text{ cgs units/cm}^2, \quad (27)$$

which is about twice that measured for potassium dihydrogen phosphate.

A Variational Principle for Scattering*

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A variational principle is presented for the phase shifts δ_l of a central force scattering problem. This generalizes the principles of Schwinger and Hulthén for S -state scattering in that (a) it is applicable to states of higher angular momentum, and (b) it depends explicitly on the "inside" wave function only. The Born approximation may be obtained with the choice of an appropriate trial function. Illustrative calculations have been made for the S - and P -state scattering states for an exponential well nucleon-nucleon interaction potential. A simple one-parameter trial function was utilized. The results are in excellent agreement with previously given exact calculations.

INTRODUCTION

THE theoretical prediction of the scattering cross section for a two-body nuclear scattering process may be reduced, as is well known, to the evaluation of the phase shifts. These are obtained from the solution of the radial part of the Schrödinger wave equation. In general, this may be a tedious numerical task, and in recent years variational procedures have been introduced by both Schwinger¹ and Hulthén² for the case of S -wave scattering which reduce the amount of labor involved. Hulthén's principle involves the phase shift explicitly, requiring an iterational procedure in solving for $k \cot \delta_0$. Hulthén has reformulated his method³ so as to avoid this difficulty, but at the expense of introducing a nonstationary element into the calculation.

In the present paper a variational expression is introduced for the phase shift which utilizes what may be called the "inside" wave function whose value is essentially nonzero only within the range of the potential well under consideration. This expression is stationary and does not involve any explicit dependence upon the

quantity sought. Because of its explicit rather than implicit dependence upon the inside wave function the present principle is an improvement over Schwinger's formulation.

Variational Principle for $k \cot \delta_l$

The radial part (u/r) of the Schrödinger wave function satisfies the equation

$$d^2u/dr^2 + [k^2 - l(l+1)/r^2 + U(r)]u = 0, \quad (1)$$

with

$$k^2 = 2mE/\hbar^2, \quad U(r) = -(2m/\hbar^2)V(r). \quad (2)$$

Here, m is the reduced mass of the two-particle system under consideration (in the case of nucleon-nucleon scattering, m equals $\frac{1}{2}$ mass of a nucleon) and E is the energy in the center-of-mass system. The variable r is the interparticle distance and $V(r)$ is the interaction potential. As usual, the constant l is the orbital angular momentum quantum number.

For scattering, the boundary conditions on $u(r)$ are

$$u(0) = 0, \quad u(\infty) = \cot \delta_l \sin(kr - \frac{1}{2}l\pi) + \cos(kr - \frac{1}{2}l\pi). \quad (3)$$

The problem under consideration is to determine the constant $\cot \delta_l$ from the solution of Eq. (1) consistent with the above boundary conditions.

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