Progress of Theoretical Physics, Vol. 35, No. 4, April 1966

Theory of Ferroelectric Phase Transition in KH_2PO_4 Type Crystals. I

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(Recieved December 6, 1965)

To explain the large isotope effect on the transition temperature in KH_2PO_4, the tunneling motion of the protons in hydrogen bonds is considered and a theory of the phase transition is developed under the assumption that the ferroelectric behavior of this substance is due to cooperation of the ionic displacements, the interactions between ions and protons and the tunneling motion of protons. The relation between the present theory and the Slater model or the Blinc model is discussed.

§ 1. Introduction

In spite of the considerable amount of investigation made from the theoretical as well as the experimental side, the microscopic mechanism of the phase transition in KH_2PO_4 and isomorphous crystals does not seem to be clearly understood. If we classify the ferroelectric substances roughly into two groups, *displacive* and *order-disorder* type ferroelectrics, then KH_2PO_4 will certainly belong to the latter group. However, the experimental data accumulated so far do not really give us a definite molecular picture of the phase transition, but sometimes reveals obvious inconsistencies among observed quantities. The main object of the present paper and a forthcoming one is to organize the somewhat divergent observed facts from the theoretical point of view and to suggest some experiments which might be helpful in attaining a full understanding of the phenomena.

The crystal structure of KH_2PO_4 (which will be abbreviated as KDP hereafter) is the so-called tetragonal diamond type. A characteristic feature of this structure is the existence of hydrogen bonds connecting two PO_4 tetrahedra, which run almost perpendicularly to the direction of the ferroelectric c axis. In the ferroelectric phase, the magnitude of the saturated polarization P_s is well accounted for by making use of the observed values for the displacements of ions K^{+1}, P^{+5} and O^{-2} along the c axis relative to their symmetric positions.[2),3)] Therefore the hydrogen bonds do not contribute any appreciable dipole moments to the saturated polarization, and hence the essential unit of the dielectric properties in this crystal is the dipole moment of the complex [K-PO_4] as shown in Fig. 1. If KDP is of an " order-disorder " type of ferroelectric, that is, if the phase transition is caused by order-disorder arrangements of the dipole moments, the two configurations of the complex [K-PO_4] denoted as (A) and

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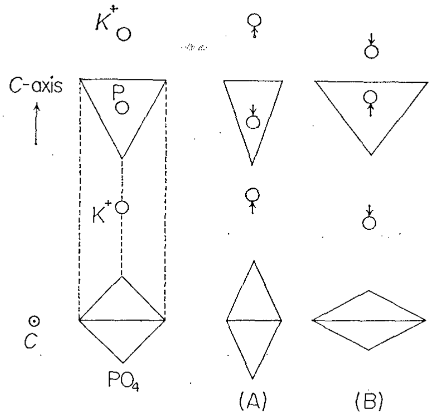

Fig. 1. The dipole unit in KH_2PO_4 and its two possible orientations.

(B) in Fig. 1 should appear with equal probability in the paraelectric phase. This presumption can be checked by X ray or neutron diffraction, but we have no definite experimental evidence on this point.

The first molecular theory of the phase transition for KDP was proposed by Slater[4] in 1941. In his theory, Slater assumes that each proton takes one of two possible positions along a hydrogen bond and in the four hydrogen bonds which are connected to a PO_4 group, only two protons occupy the positions nearer to the PO_4. All other configurations in which protons more than two or less than two are attached to one PO_4 group, are assumed to have higher configuration energy and are discarded. The polarization of the unit cell may be determined from the proton configurations and a state of complete order in the proton arrangement is assumed to correspond to the ferroelectric ground state. This model has subsequently obtained experimental support from the neutron diffraction work carried out by Bacon et al.,[2] who showed that the proton density distribution deduced from the neutron diffraction extends along the hydrogen bond in the paraelectric phase, and becomes localized around an asymmetric position shifted from the center of the bond in the ferroelectric phase. The direction of the proton shift from the center of the bond is reversed when the applied field is reversed. Thus the view that the phase transition in KDP is triggered by the order-disorder transition in the proton arrangement seems to be established. The Slater model can provide a good account of the observed entropy change at the Curie temperature, although the predicted phase change is not of the second kind as is actually observed. By taking account of the proton configurations discarded in the Slater model, Takagi showed that the phase transition may be of the second kind and the agreement between theory and experiment on thermodynamical and dielectric properties is much improved.[5] More recently, a refinement of the theory along the lines of the Slater-Takagi model has been given by Silsbee et al.[6]

Though the Slater-Takagi theories are successful in explaining many properties of KDP, they have a serious defect. A remarkable feature of the phase transition in KDP is the very large isotope effect. On deuteration, the Curie temperature T_c of KH_2PO_4[7] is raised by as much as 1.7 times, whereas the Curie constant C does not change very much.[8] Concerning the isotope effect on the saturated polarization P_s, two different results have been reported: Bantle,[9] from the hysteresis loop, finds no isotope effect, while Zwicker and Scherrer[10] observe an isotope effect from their electro-optical measurement. According to the Slater type of theory, however, the Curie temperature T_c depends solely on ε, the energy difference between two different configurations of PO_4 with respect to the two proton attachments (see Fig. 3), and it would be very hard to assume that ε has a strong dependence on the proton mass.

In order to explain the large isotope effect, Pirrene[11] proposes, in opposition to the Slater theory, another model in which the kinetic energy of the protons plays an important role. Pirrene's idea is further developed by Blinc[12] in a model in which the proton is assumed to make a tunneling motion between two minima of the potential along the hydrogen bond. It is evident that the tunneling motion of the proton opposes the tendency to attain the lower energy configuration and that the lighter the particle is, the more easily it can tunnel, thus inhibiting the phase transition. Thus we can expect a higher Curie temperature on deuteration. If the proton tunneling really takes place, it should give rise to a splitting in the vibrational level of the proton. Blinc and Hadzi[13] have found the expected splitting of the vibrational levels by analyzing their infrared absorption data for KDP and its isomorphs. But Razarev et al.[14] have questioned Blinc and Hadzi's interpretation of their experiments. More direct evidence for the existence of the splitting might be obtained by observing the light quanta emitted when vibrational transitions between the levels of the doublet takes place, which would probably fall in the far infrared region. Hadzi[15] claims that he has observed these light quantum in his experiments, whereas Tinkam and his co-workers[16] question his result. Besides these controversial points, there is another experimental fact unfavourable to the Blinc model. Although Blinc has not discussed the dynamical properties in the light of his model, it is expected that his model gives a dielectric dispersion of a resonance type. According to a recent measurement by Hill and Ichiki,[17] however, the dielectric dispersion of KD_2PO_4 is rather of the Debye type, with distributed relaxation times.

In spite of these unclear points, we shall still examine the Blinc model by generalizing it to some extent and by asking whether this generalized version of the Blinc can do better than other models in giving a consistent account of various experimental facts. The viewpoint we take in this paper is the following. We assume that the large isotope effect in KDP is due to the proton motion and hence there exists proton tunneling. On the other hand, the phase transition is assumed to be triggered by a cooperative ordering in the proton arrangement, to which the displacements of ions are strongly coupled. Thus the ferroelectric behavior of KDP is due to the combined effect of several different factors—the ionic displacements, interaction between ions and protons and the kinetic energy of protons. In § 2 we set up a Hamiltonian which can describe the different degrees of freedom and their interactions. Further reduction and simplification of the Hamiltonian is made to focus our attention on the proton system and to discuss the influence of the proton motion on the order-disorder transition in the proton arrangements. In § 3 we neglect the tunneling effect in the Hamiltonian set up in § 2 and look for the relation between our Hamiltonian and the Slater-Takagi model, so that we may identify some of the parameters involved in our Hamiltonian with those used in previous theories. Then we work out a Bethe approximation to discuss the temperature dependence of the spontaneous polarization and other quantities. Section 4 is devoted to the explanation of the isotope effect with the aid of a simplified Hamiltonian. The present calculation can reproduce the essential features of the Blinc theory of the isotope effect, but in addition it enables us to discuss the consistency of the isotope effects observed for the Curie temperature T_c, the magnitude of the saturated polarization P_s and the Curie constant C. The concentration dependence of T_c in partially deuterated crystals is also investigated from our new point of view in connection with a recent measurement by Kaminow.[18] In § 5 we summarize the results of the calculations and criticize the Blinc model. Dynamical problems such as dielectric relaxation and inelastic scattering of neutrons will be discussed in a forthcoming paper.

§ 2. Effective Hamiltonian[*]

First we shall follow Slater's idea that the dielectric properties of KDP may be entirely determined by the proton configuration. Of course this is an approximation and we shall make the necessary generalization later so as to include the other degrees of freedom such as the dipoles caused by ionic displacements. A projection of the network of hydrogen bonds on a plane perpendicular to the c axis is shown in Fig. 2. Each proton represented by a small circle has two equilibrium positions along a bond which connects two PO_4 groups represented by the tetrahedra, and executes anharmonic oscillation in a double-minimum potential. Let us enumerate all the protons in a definite order. Then we assume that the energy of the proton system is expressed in the form

$$H_{\text{proton}} = \sum_i H_1(i) + \sum_{i>j}\sum H_2(ij) + \cdots, \quad (2\cdot1)$$

where $H_1(i)$ represents the part of the energy which depends only on the configuration of the i-th proton and $H_2(ij)$ the part which depends on the pair configuration of the i-th and j-th protons and so forth.

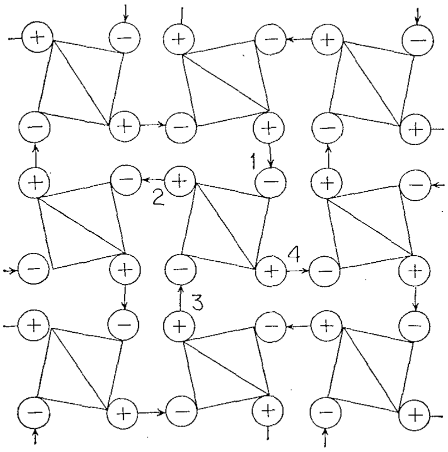

Fig. 2. A projection of the network of hydrogen bonds on a plane perpendicular to the c axis. + and − denote two possible sites for the proton.

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[*] The idea described in this section has been reported at the symposium on the "phase transition and ferroelectrics" which was held in January, 1962, at the Research Institute for Solid State Physics. Essentially the same idea was also published by de Gennes in 1963.[19]

We shall neglect all interactions of higher order than H_2. Since we are going to put special emphasis on the tunneling of the proton between two stable positions, it turns out to be convenient to adopt the second qnantization formalism for the proton system, although the Fermi statistics of the proton does not play any important role in the present problem. Let $\Psi(r)$ be the quantized wave function for the protons, then the Hamiltonian H_{proton} may be expressed as

$$H_{\text{proton}}=\int\Psi^*(r)H_1\Psi(r)\,dr+(1/2)\int\int\Psi^*(r)\Psi^*(r')H_2\Psi(r')\Psi(r)\,drdr'.$$

The protons are highly localized along the hydrogen bonds, and hence we can choose a properly complete set of localized wave functions as the basis for the expansion of $\Psi(r)$. We denote the ground state wave function of the i-th proton which is oscillating around one of two stable positions along the i-th hydrogen bond by $\phi_i^a(r)$ or $\phi_i^b(r)$ according as the equilibrium position is the + site or the − site as shown in Fig. 2. In general, we have to consider all the wave functions of higher excited states, but there is some experimental evidence that such excited states are not important except for temperatures higher than those we are considering here.[13),20)] We shall ignore them for the sake of simplicity. Assuming that the set of functions $\{\phi_i^\mu(r),\ \mu=a \text{ or } b,\ i=1,\cdots 2N\}$ are already made orthogonal to each other, we expand $\Psi(r)$ in the form

$$\Psi(r)=\sum_i\{a_i\,\phi_i^a(r)+b_i\,\phi_i^b(r)\}\ , \tag{2·2}$$

where the expansion coefficients a_i and b_i are Fermi operators which satisfy the well-known commutation relations

$$\begin{aligned}&[a_i^*,\ a_j]_+=[b_i^*,\ b_j]_+=\delta_{ij}\\&[a_i,\ a_j]_+=[a_i^*,\ a_j^*]_+=[b_i,\ b_j]_+=[b_i^*,\ b_j^*]_+=0\\&[a_i,\ b_j]_+=[a_i^*,\ b_j]_+=[a_i,\ b_j^*]_+=[a_i^*,\ b_j^*]_+=0\,.\end{aligned}\tag{2·3}$$

If we put (2·2) into H_{proton}, there appear many kinds of combinations of products in a quadratic form for H_1 and in a quartic form for H_2. However, since the $\phi_i^\mu(r)$'s are localized functions, we may safely neglect the overlapping of them except for that of the form

$$\phi_i^a(r)\ \phi_i^b(r)\ .$$

This assumption simplifies the results, and the relevant terms in H_{proton} become

$$\begin{aligned}H_{\text{proton}}=&\sum_i[h(aa)a_i^*a_i+h(bb)b_i^*b_i+h(ab)(a_i^*b_i+b_i^*a_i)]\\&+(1/2)\sum_{ij}[V_{ij}(aa,\ aa)a_i^*a_j^*a_ja_i+V_{ij}(bb,\ bb)b_i^*b_j^*b_jb_i\\&\qquad+V_{ij}(aa,\ bb)(a_i^*b_j^*b_ja_i+b_i^*a_j^*a_jb_i)\\&+V_{ij}(ab,\ aa)(a_i^*a_j^*a_jb_i+a_i^*a_j^*b_ja_i+a_i^*b_j^*a_ja_i+b_i^*a_j^*a_ja_i)\end{aligned}\tag{2·4}$$

$$+V_{ij}(ab,\,ab)\,(a_i{}^*a_j{}^*b_jb_i+a_i{}^*b_j{}^*a_jb_i+b_i{}^*b_j{}^*a_ja_i+b_i{}^*a_j{}^*b_ja_i)$$
$$+V_{ij}(ab,\,bb)\,(a_i{}^*b_j{}^*b_jb_i+b_i{}^*a_j{}^*b_jb_i+b_i{}^*b_j{}^*a_jb_i+b_i{}^*b_j{}^*b_ja_i)]\ ,$$

where

$$h(\mu\nu)=\int\phi_i{}^\mu(r)\,H_1(i)\,\phi_i{}^\nu(r)\,dr \tag{2·5}$$

and

$$V_{ij}(\mu\nu,\,\alpha\beta)=\int\int\phi_i{}^\mu(r)\,\phi_j{}^\alpha(r')\,H_2(ij)\,\phi_j{}^\beta(r')\,\phi_i{}^\nu(r)\,dr\,dr'\ , \tag{2·6}$$

μ, ν, α and β being either a or b. We assume that a proton occupies definitely either one of two equilibrium positions along a bond and therefore

$$a_i{}^*a_i+b_i{}^*b_i=1\ . \tag{2·7}$$

With this restriction, the products of a creation operator and an annihilation operator at the same site can be replaced by equivalent spin operators. To be more precise, it can be shown that the operators defined by

$$\begin{aligned}Z_i&=(1/2)\,(a_i{}^*a_i-b_i{}^*b_i)\quad ,\\ X_i&=(1/2)\,(a_i{}^*b_i+b_i{}^*a_i)\quad ,\\ Y_i&=(1/2i)\,(a_i{}^*b_i-b_i{}^*a_i)\end{aligned} \tag{2·8}$$

satisfy the commutation relations for spin operators

$$[X_i,\,Y_j]_-=i\delta_{ij}Z_i,\quad [Y_i,\,Z_j]_-=i\delta_{ij}X_i,\quad [Z_i,\,X_j]_-=i\delta_{ij}Y_i. \tag{2·9}$$

In terms of these operators, (2·4) can be rewritten as

$$\begin{aligned}H_{\mathrm{proton}}=&\sum_i\left[\frac{1}{2}\{h(aa)+h(bb)\}+\{h(aa)-h(bb)\}Z_i+2h(ab)\,X_i\right]\\ &+(1/2)\sum_{ij}\Big[V_{ij}(aa,\,aa)\left(\frac{1}{2}+Z_i\right)\left(\frac{1}{2}+Z_j\right)+V_{ij}(bb,\,bb)\left(\frac{1}{2}-Z_i\right)\left(\frac{1}{2}-Z_j\right)\\ &+V_{ij}(aa,\,bb)\left\{\left(\frac{1}{2}+Z_i\right)\left(\frac{1}{2}-Z_j\right)+\left(\frac{1}{2}-Z_i\right)\left(\frac{1}{2}+Z_j\right)\right\}\\ &+V_{ij}(ab,\,aa)\,\{(1+2Z_i)\,X_j+X_i(1+2Z_j)\}+4V_{ij}(ab,\,ab)\,X_iX_j\\ &+V_{ij}(ab,\,bb)\,\{X_i(1-2Z_j)+(1-2Z_i)\,X_j\}\Big]\ .\end{aligned} \tag{2·10}$$

From symmetry considerations it is required that

$$h(aa)=h(bb)$$

and

$$V_{ij}(aa,\,aa)=V_{ij}(bb,\,bb)\ .$$

Then rearranging the various terms in (2·10) and omitting the constant terms, we obtain an effective Hamiltonian for the proton system in the form

$$H_{\text{proton}}=-2\Omega\sum_i X_i-(1/2)\sum_{ij}[J_{ij}Z_iZ_j+L_{ij}(X_iZ_j+Z_iX_j)+K_{ij}X_iX_j]\ , \qquad (2\cdot 11)$$

where the coefficients 2Ω, J_{ij}, L_{ij} and K_{ij} are given by

$$\begin{aligned}-2\Omega&=2h(ab)+(1/2)\sum_j[V_{ij}(ab,\,aa)+V_{ji}(ab,\,aa)+V_{ij}(ab,\,bb)+V_{ji}(ab,\,bb)]\ ,\\ J_{ij}&=2V_{ij}(aa,\,bb)-V_{ij}(aa,\,aa)-V_{ij}(bb,\,bb)\ ,\\ L_{ij}&=2V_{ij}(ab,\,bb)-2V_{ij}(ab,\,aa)\ , \qquad (2\cdot 12)\\ K_{ij}&=-4V_{ij}(ab,\,ab)\ .\end{aligned}$$

It is not hard to give a physical meaning to each term in the Hamiltonian (2·11). The two possible directions of the i-th "spin" Z_i correspond obviously to the two possible equilibrium positions of the i-th proton, and the x component of the i-th "spin" X_i makes the i-th proton jump from the + site to the − site and vice versa. Therefore the first term in the right-hand side of (2·11) represents the kinetic energy. The second term is the interaction energy between protons and the third and fourth terms are connected with the effects caused by interference between the tunneling motion and proton interaction. However, the last two terms may be ignored because they are proportional to integrals which involve the products of the wave functions localized at different equilibrium positions. In a later section we shall base our discussion on a simplified Hamiltonian

$$H=-2\Omega\sum_i X_i-(1/2)\sum_{ij} J_{ij}Z_iZ_j, \qquad (2\cdot 13)$$

under the assumption that L_{ij} and K_{ij} are much smaller than J_{ij}.

It will be appropriate to make two remarks at this point. First, the main part of 2Ω is the so-called resonance integral $h(ab)$ which depends on the proton mass. Assuming a harmonic oscillator wave function, Blinc has given an approximate expression for $h(ab)$.[13] Generally speaking, $h(ab)$ becomes smaller when the mass of the oscillator is increased. Secondly, within the framework of the Slater model the dipole moment of a PO_4 group is determined by the configuration of the four protons attached to it. This means that the dipole moment is a function of the spin variables Z_i. If we define the + and − positions of each proton as indicated in Fig. 2, then the Slater model tells us that the c component of the total polarization is proportional to

$$P=\mu\sum_i Z_i\ , \qquad (2\cdot 14)$$

where μ denotes the magnitude of a dipole moment associated with a complex [K-H_2PO_4]. When we cosider the Blinc model, the total polarization will fluctuate as the proton tunneling takes place. So long as we take P given by (2·14) as the total polarization of the crystal, we are assuming that the time variation of P follows the proton motion instantaneously.

As was stated in the introduction, it seems that the polarization of the crystal lattice results not from the proton charges but from the displacements of the ions K^{+1}, P^{+5} and O^{-2}. Therefore it is more realistic to introduce the degree of freedom associated with the ionic displacements in addition to those of the proton system. Instead of going into a detailed discussion of the introduction of this new degree of freedom, we shall content ourselves with a slight extension of the theory described so far. We suppose that the crystal is composed of N dipole moments strongly coupled to the proton system. Each dipole is assumed to take only two alternative directions which are represented by two values of an Ising spin σ_n, n being the suffix denoting the position of each dipole. The above assumption is not unreasonable in view of the fact that the spontaneous polarization in the ferroelectric phase is closely connected with a definite displacement of the complex [K-PO$_4$] along the ± c directions. The two values of σ correspond to the two configurations A and B of the complex [K-PO$_4$] shown in Fig. 1. The energy of the crystal is a function of the configurations of both dipoles and protons. Let us assume a Hamiltonian of the following form:

$$H = -(\mu^2/2)\sum_{n n'} \sigma_n G_{n n'} \sigma_{n'} - \mu E \sum_n \sigma_n - \sum_n V_n(\sigma_n, [r_i]_n) + \sum_i H_1(i) . \quad (2\cdot 15)$$

In this expression the first term represents the dipole-dipole interaction and the second term is the potential energy of the dipoles in an external field E. In the third term $V_n(\sigma_n, [r_i]_n)$ is the energy of the n-th dipole in the field produced by the surrounding protons whose coordinates are denoted by the symbol $[r_i]_n$. $H_1(i)$ is the part of energy which depends only on the configurations of the i-th proton. H_1 can be expressed in terms of the x component of "spin" X_i. In order to express the third term in terms of spin operators, we first expand V_n as

$$V_n(\sigma_n, [r_i]_n) = \frac{1}{2}(1+\sigma_n) V_+([r_i]_n) + \frac{1}{2}(1-\sigma_n) V_-([r_i]_n) .$$

V_+ and V_- are now expressed in terms of spin operators in a similar way as before and if we retain only the pair type interactions for the sake of simplicity, the final result takes the form

$$\begin{aligned} V_n(\sigma_n, [r_i]_n) = -\sum_n \frac{1+\sigma_n}{2} \Big[\sum_{ij} \{ & J_{ij}^n(+) Z_i Z_j + K_{ij}^n(+) X_i X_j \\ & + L_{ij}^n(+)(X_i Z_j + Z_i X_j)\} + \sum_i \{v_{ni}(+) Z_i + \omega_{ni}(+) X_i\}\Big] \qquad (2\cdot 16) \\ & - \sum_n \frac{1-\sigma_n}{2} [(+) \to (-)] . \end{aligned}$$

The last line in (2·16) is the expression occurring in the first two lines but with all $(+)$ replaced by $(-)$. From the fact that the configuration with $\sigma_n = 1$ and

$Z_i=1/2$ has the same energy as the configuration with $\sigma_n=-1$ and $Z_i=-1/2$, it is required that

$$\begin{aligned} &J^n_{ij}(+)=J^n_{ij}(-)=J^n_{ij}\,, \\ &K^n_{ij}(+)=K^n_{ij}(-)=K^n_{ij}\,, \\ &L^n_{ij}(+)=-L^n_{ij}(-)=L^n_{ij}\,, \\ &v_{ni}(+)=-v_{ni}(-)=v_{ni}\,, \\ &\omega_{ni}(+)=\omega_{ni}(-)=\omega_{ni}\,. \end{aligned} \tag{2·17}$$

By making use of these relations, (2·16) may be rewritten as

$$\begin{aligned} V_n(\sigma_n,\,[r_i]_n)=&-(1/2)\sum_{ij}\,[J_{ij}Z_iZ_j+K_{ij}X_iX_j]-\sum_i\omega_iX_i \\ &-\sum_n\sum_{ij}L^n_{ij}\sigma_n(X_iZ_j+Z_iX_j)-\sum_{ni}v_{ni}\sigma_nZ_i\,, \end{aligned} \tag{2·18}$$

where the following abbreviations have been used:

$$J_{ij}=\sum_n J^n_{ij},\quad K_{ij}=\sum_n K^n_{ij},\quad \omega_i=\sum_n\omega_{ni}\,. \tag{2·19}$$

Adding the dipole-dipole interaction, the field energy and the kinetic energy of protons to (2·18), we have finally the total Hamiltonian

$$\begin{aligned} H=&-(\mu^2/2)\sum_{nn'}\sigma_nG_{nn'}\sigma_{n'}-\mu E\sum_n\sigma_n-2\Omega\sum_i X_i-(1/2)\sum_{ij}\,[J_{ij}Z_iZ_j+K_{ij}X_iX_j] \\ &-\sum_n\sum_{ij}L^n_{ij}\sigma_n(Z_iX_j+X_iZ_j)-\sum_{ni}v_{ni}\sigma_nZ_i\,, \end{aligned} \tag{2·20}$$

where 2Ω is a sum of the resonance integral $h(ab)$ and ω_i. K_{ij} and L^n_{ij} are much smaller than J_{ij} and may be discarded. In the derivation of (2·20) we have made a number of assumptions and simplifications. A more elaborate calculation, however, leads to essentially the same result as the above Hamiltonian except for higher order terms.

§ 3. Relation to the Slater-Takagi model

In this section we shall study the relation between the effective Hamiltonian derived in § 2 and the Slater-Takagi model. For this purpose we omit the tunneling effect and start with

$$H=-(1/2)\sum_{ij}J_{ij}Z_iZ_j\,. \tag{3·1}$$

To clarify the relation between (3·1) and the Slater model, it is convenient to consider the energy levels of one PO_4 group determined by four proton configurations. Let us take a PO_4 and four protons attached to it and denote their spin variables by Z_1, Z_2, Z_3 and Z_4 as shown in Fig. 2. If we retain the interactions J_{ij} only between nearest neighbours, then there appear two interaction parameters

$$U = J_{13} = J_{24}$$

and

$$V = J_{12} = J_{34} = J_{23} = J_{14} . \qquad (3\cdot 2)$$

In the present model, one PO_4 group can take 2^4 different configurations depending on the set of values $\{Z_j = \pm 1/2,\ j = 1, \cdots 4\}$. Using $(3\cdot 1)$ and $(3\cdot 2)$, the energy level of each state can easily be calculated and the results are summarized in Table I. Instead of U and V, we define two parameters ε_0 and ε_1 by

Table I. Energy levels of a PO_4.

configuration Z_1 Z_2 Z_3 Z_4	number of protons attached to PO_4	configuration Z_1 Z_2 Z_3 Z_4	number of protons attached to PO_4	energy
+ + + +	2	− − − −	2	$-(2U+4V)/4$
+ − + −	2	− + − +	2	$U/2$
+ − − +	2	− + + −	2	
+ + + −	3	− − − +	1	0
+ + − +	3	− − + −	1	
+ − − −	3	− + + +	1	
+ − + +	1	− + − −	3	
+ + − −	4	− − + +	0	$-(2U-4V)/4$

$$U = -2\varepsilon_1 , \qquad (3\cdot 3)$$
$$V = 2\varepsilon_1 + \varepsilon_0 ,$$

and adjusting the zero of energy so that the energy of the configuration $(++++)$ or $(----)$ becomers zero, we obtain the level scheme depicted in Fig. 3. The energy levels assumed in the Slater model and in the Takagi model are also given in the same figure. The Slater model corresponds to taking ε_1 as infinity, while in the Takagi model the highest level in Fig. 3 is discarded (i.e. $\varepsilon_0 + 3\varepsilon_1 \to \infty$).

It is instructive to study the thermodynamical properties of the system with the Hamiltonian $(3\cdot 1)$ using the cluster approximation. Let us take a cluster of four protons Z_j, $j = 1, 2, 3, 4$, and let the Hamiltonian of this cluster be

$$H_4 = -U(Z_1Z_2 + Z_2Z_4) - V(Z_1Z_2 + Z_1Z_4 + Z_2Z_3 + Z_3Z_4)$$
$$- [\mu E + (U + 2V)\bar{Z}](Z_1 + Z_2 + Z_3 + Z_4) , \qquad (3\cdot 4)$$

where $\bar{Z}$ is the statistical average of Z_j for a proton outside the cluster. Similarly we denote the Hamiltonian of a proton $j = 1$ in the molecular field of the other protons as

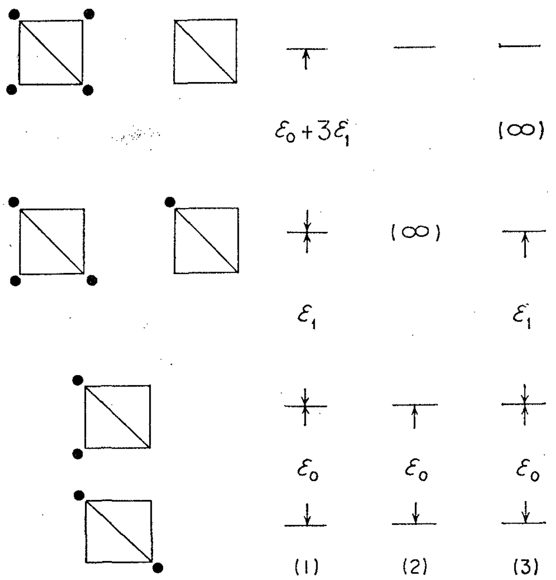

Fig. 3. Energy levels of PO_4 for various models.
(1) present model
(2) Slater model
(3) Takagi model

$$H_1=-[\mu E+(2U+4V)\bar{Z}]Z_1\,. \tag{3·5}$$

Further we introduce the density matrices of the cluster and one proton by

$$\rho_4(1,2,3,4)=\frac{\exp[-\beta H_4]}{\mathrm{Tr}(\exp[-\beta H_4])}\,, \tag{3·6}$$

$$\rho_1(1)=\frac{\exp[-\beta H_1]}{\mathrm{Tr}(\exp[-\beta H_1])}\,.$$

The cluster approximation is equivalent to demanding that the $\bar{Z}$ appearing both in H_1 and H_4 are the same, and hence

$$\mathrm{Tr}_{2,3,4}\rho_4(1,2,3,4)=\rho_1(1)\,, \tag{3·7}$$

where $\mathrm{Tr}_{2,3,4}$ means a partial trace over the variables Z_2, Z_3 and Z_4. For the case of no external field ($E=0$), the values of the Boltzmann factor $\exp[-\beta H_4]$ are listed in Table II for various configurations. In this Table II, a, b and c are defined respectively by

Table II. Boltzmann factors for various cluster configurations.

configuration				degeneracy	Boltzmann factor	dipole moment
Z_1	Z_2	Z_3	Z_4			
+	+	+	+	1	c^4	$+2\mu$
−	−	−	−	1	c^{-4}	-2μ
+	−	+	−	4	a	0
+	+	+	−	4	abc^2	$+\mu$
−	−	−	+	4	abc^{-2}	$-\mu$
+	+	−	−	2	a^2b^4	0

$$\begin{aligned} a&=\exp(-\beta\varepsilon_0)\,,\\ b&=\exp(-\beta\varepsilon_1)\,,\\ c&=\exp[-\beta(U+2V)\bar{Z}/4]\,. \end{aligned} \tag{3·8}$$

Now it is an easy task to write down the matrix elements of equation (3·7), which has a diagonal form. Thus for $Z_1=1/2$ we have

$$\mathcal{Z}_4^{-1}(K+3Lc^2+Lc^{-2}+c^4)=\mathcal{Z}_1^{-1}c^2 \tag{3·9}$$

and for $Z_1=-1/2$

$$\mathscr{Z}_4^{-1}(K+3Lc^{-2}+Lc^2+c^{-4})=\mathscr{Z}_1^{-1}c^{-2}, \tag{3·10}$$

where the following abbreviations have been introduced:

$$\mathscr{Z}_1=c^2+c^{-2}, \tag{3·11a}$$

$$\mathscr{Z}_4=c^4+c^{-4}+4L(c^2+c^{-2})+2K, \tag{3·11b}$$

$$K=2a+a^2b^4, \tag{3·11c}$$

$$L=ab. \tag{3·11d}$$

An equation which determines $\bar{Z}$ or c as a function of temperature is obtained by subtracting (3·10) from (3·9):

$$\frac{(c^2-c^{-2})\,[2L+(c^2+c^{-2})]}{c^4+c^{-4}+4L(c^2+c^{-2})+2K}=\frac{c^2-c^{-2}}{c^2+c^{-2}}. \tag{3·12}$$

It is obvious that equation (3·12) always has a solution

$$c=1 \quad \text{or} \quad \bar{Z}=0. \tag{3·13}$$

Besides this solution, which describes the disordered state, there exists another solution

$$1-K=L(c^2+c^{-2}), \tag{3·14}$$

provided that the temperature T is lower than a critical temperature T_c determined from

$$1-K(\beta_c)=2L(\beta_c), \qquad \beta_c=1/kT_c. \tag{3·15}$$

For $T<T_c$ the solution with non-zero $\bar{Z}$ provides us with a stable solution, and the value of $\bar{Z}$ is related to the spontaneous polarization P_s in the following manner. If we define the dipole moment of one PO_4 group as a function of the proton configurations as is shown in the last column of Table II, then the spontaneous polarization P_s is given by

$$P_s=2N\mu\bar{Z}=2N\mu\,\mathrm{Tr}[Z_1\,\rho_1(1)] \tag{3·16}$$

which, in virtue of (3·8), (3·11) and (3·14), turns out to be

$$P_s=N\mu\frac{[(1-K+2L)(1-K-2L)]^{1/2}}{1-K}. \tag{3·17}$$

In Fig. 4 the curves of $P_s/N\mu$ calculated from (3·17) are shown as functions of T/T_c for various values of the ratio $\varepsilon_1/\varepsilon_0=n$. As is seen from this figure, the phase transition becomes much sharper as n is increased, and in the limit of $n\to\infty$ the transition is of the first order. The results obtained here are very similar to those of the Takagi model, but different in an important respect from those obtained by ter Haar and Grindley,[21] who worked out a similar theory of the phase transition in KDP. They obtained a result in which the order of the phase transition may change from the second order to the first order depending on the magnitude of the interaction parameters J_{ij}. The origin of the discrepancy between the present theory and theirs can be readily traced back to an inadequacy in the assumptions made about the energy levels of a PO_4 group in their model.

Performing a similar calculation for the case of a finite field ($E \neq 0$), we can easily derive an expression for the electric susceptibility. We shall mention here only the results. For $T > T_c$

$$\chi = \frac{N\mu^2}{kT} \cdot \frac{L+1}{K+2L-1} \tag{3·18}$$

and for $T < T_c$

$$\chi = \frac{N\mu^2}{kT} \left(\frac{2L}{1-K} \right)^2 \frac{K+4L-1}{2(1-K-2L)} . \tag{3·19}$$

If we let $\varepsilon_1 \to \infty$ in (3·15) and (3·18), we recover Slater's results

$$T_c = \varepsilon_0 / k \log 2 \tag{3·20}$$

and

$$\chi = \frac{N\mu^2}{kT} \frac{1}{2\exp(-\beta\varepsilon_0) - 1} . \tag{3·21}$$

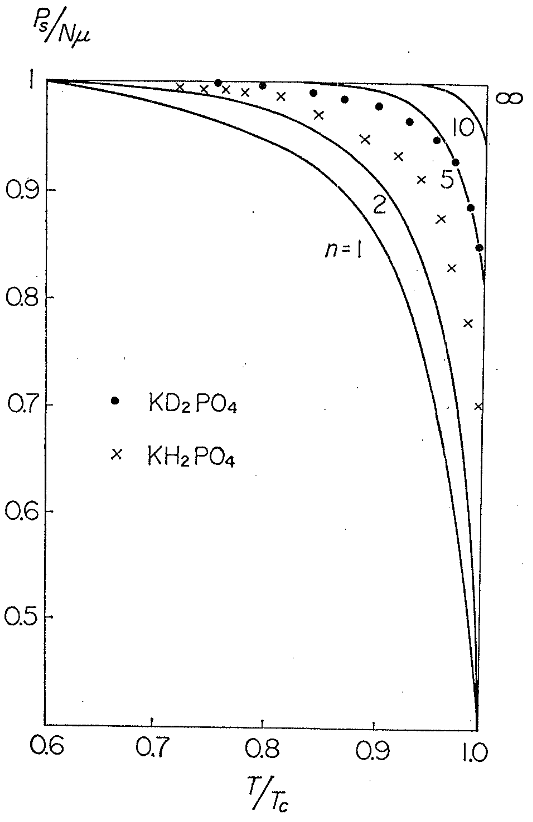

Fig. 4. $P_s/N\mu$ as the functions of T/T_c for various values of $n = \varepsilon_1/\varepsilon_0$. ● and × represent the experimental values.

§ 4. Isotope effect

We are now in a position to discuss the isotope effect using the tunneling model. First we start with the Hamiltonian (2·13)

$$H = -2\Omega \sum_i X_i - (1/2) \sum_{ij} J_{ij} Z_i Z_j$$

and adopt a molecular field approximation. Introducing an external and a molecular field, we replace the original Hamiltonian by

$$H = -\sum_i \left[2\Omega X_i + J\bar{Z} Z_i + \mu E Z_i \right] , \tag{4·1}$$

where $J = \sum_j J_{ij}$ and $\bar{Z}$ is the thermal average of Z, a quantity to be determined self-consistently at a later stage. The eigenvalues of (4·1) are readily found to be

$$W_E = \pm \frac{1}{2}\left[(2\Omega)^2 + (J\bar{Z}+\mu E)^2\right]^{1/2} \tag{4·2}$$

and the partition function per proton is thus given by

$$\mathcal{Z} = 2\cosh(\beta W_E)\,. \tag{4·3}$$

The self-consistency condition will be fulfilled if $\bar{Z}$ is determined from an equation

$$\bar{Z} = \partial/\partial(\beta J\bar{Z})\log\mathcal{Z}\,, \tag{4·4}$$

which gives us

$$\bar{Z} = (J\bar{Z}+\mu E)/2W_E\cdot\tanh(\beta W_E)\,. \tag{4·5}$$

In the case $E=0$, (4·5) has always a solution $\bar{Z}=0$. Besides this solution, when the temperature is sufficiently low we have another solution determined from

$$2\left[(2\Omega)^2+(J\bar{Z})^2\right]^{1/2}/J = \tanh\left[\beta\sqrt{(2\Omega)^2+(J\bar{Z})^2}/2\right]. \tag{4·6}$$

The critical temperature T_c is given by an equation

$$4\Omega/J = \tanh(\Omega/kT_c)$$

or

$$kT_c = (J/4)\,(q/\tanh^{-1}q) \tag{4·7}$$

with $q=4\Omega/J$. $\bar{Z}$ is proportional to the spontaneous polarization P_s and the maximum value of P_s attained at $T=0$ can be shown to be

$$P_M = 2N\mu\,\bar{Z}_{T=0} = N\mu(1-q^2)^{1/2}\,. \tag{4·8}$$

The expression for the electric susceptibility χ is also easily derived by working out a similar calculation with the finite field E. The result is, for $T>T_c$,

$$\chi = \frac{N\mu^2}{kT}\cdot\frac{1}{\coth(\beta\Omega)-\coth(\beta_c\Omega)}\,. \tag{4·9}$$

We are ready to study the isotope effect by making use of these formulae. We assume that deuteration changes only the parameter Ω and does not influence N, μ and J. Let us call the ratio of the value of Ω for deuteron and proton

$$p = \Omega^D/\Omega^H\,. \tag{4·10}$$

Then the ratios of the critical temperature, and the maximum polarization for KD_2PO_4 and KH_2PO_4 are respectively given by

$$T_c^D/T_c^H = p\left[\tanh^{-1}q/\tanh^{-1}(pq)\right] \tag{4·11}$$

and

$$P_M^D/P_M^H = \left[1-(pq)^2\right]^{1/2}/\left[1-q^2\right]^{1/2}\,. \tag{4·12}$$

In Fig. 5 the calculated curves for the ratio T_c^D/T_c^H are shown as the functions of q for several p values. The observed values for five isomorphous crystals are also indicated by horizontal lines in the same figure. In order to get agreement between theory and experiment, a rather high value of q is required. In the case of KDP, for instance, we have to take $q=0.92$ even if $p=0$. This q value, which is necessary to explain the isotope effect on the transition temperature, however, gives an isotope effect on the ratio of the maximum spontaneous polarizations given by (4·12) too large to be compared with the observed value. Furthermore, the temperature variation of the susceptibility just above T_c predicted from (4·9), is quite sensitive to the change of Ω, in contradiction with the observed behavior. Thus we encounter difficulty so long as we adopt the Hamiltonian (4·1).

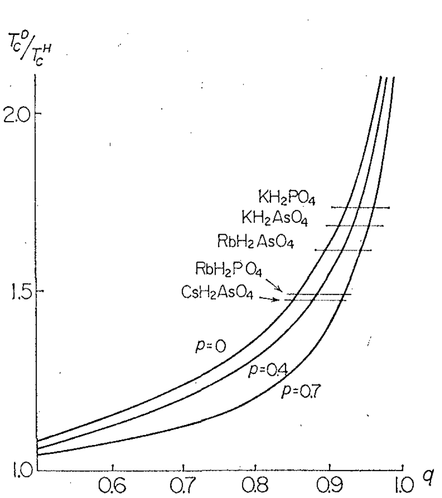

Fig. 5. Calculated curves for the ratio T_c^D/T_c^H as the functions of q and p. Horizontal lines represent observed values for different isomorphous crystals.

The molecular field approximation is by no means adequate in the present problem because it fails to take into account the strong short range correlation among the four protons near one PO_4 group. This defect of the molecular field approximation is most clearly manifested in the fact that the critical temperature in this approximation is determined (when $q=0$) by

$$kT_c = J/4 = \varepsilon_0 + \varepsilon_1 , \tag{4·13}$$

which is in remarkable contrast to the cluster approximation described in § 3 where in the limit of $\varepsilon_1 \to \infty$ kT_c was given by $\varepsilon_0/\log 2$. Therefore it is desirable to work out a theory of the isotope effect based on the cluster approximation. To do this, we include the kinetic energy of protons in the Hamiltonian (3·4) in the form

$$\begin{aligned} H_4 = & -U(Z_1Z_3+Z_2Z_4) - V(Z_1Z_2+Z_1Z_4+Z_2Z_3+Z_3Z_4) \\ & -\zeta(Z_1+Z_2+Z_3+Z_4) - 2\Omega(X_1+X_2+X_3+X_4) \end{aligned} \tag{4·14}$$

and in (3·5) in the form

$$H_1 = -2\zeta Z_1 - 2\Omega X_1 , \tag{4·15}$$

where we omit the external field E and put

$$\zeta = (U+2V)\bar{Z} . \tag{4·16}$$

The principle of the calculation is the same as before and the self-consistent equation to determine $\bar{Z}$ is, instead of (3·12), given by

$$\frac{\partial}{\partial(\beta\zeta)} \log \mathcal{Z}_4 = 2\frac{\partial}{\partial(\beta\zeta)} \log \mathcal{Z}_1 \qquad (4\cdot17)$$

with

$$\mathcal{Z}_4 = \mathrm{Tr}[\exp(-\beta H_4)] \qquad (4\cdot18\mathrm{a})$$

and

$$\mathcal{Z}_1 = \mathrm{Tr}[\exp(-\beta H_1)]\ . \qquad (4\cdot18\mathrm{b})$$

Actual evaluation of (4·17) is difficult, but the determination of the transition temperature can be made without much trouble by expanding both sides of (4·17) in powers of ζ and equating the first terms on both sides. In this way, T_c is determined as a function of ε_0, $n=\varepsilon_1/\varepsilon_0$ and $q=\Omega/\varepsilon_0$. Figure 6 shows $T_c(q)/T_c(q=0)$ as a function of q for the case $n=5$. If we assume that there exists no tunneling motion KD_2PO_4, i.e. $q=0$, then the observed isotope effect on T_c in KH_2PO_4 may be accounted for by taking $q=1.4$.

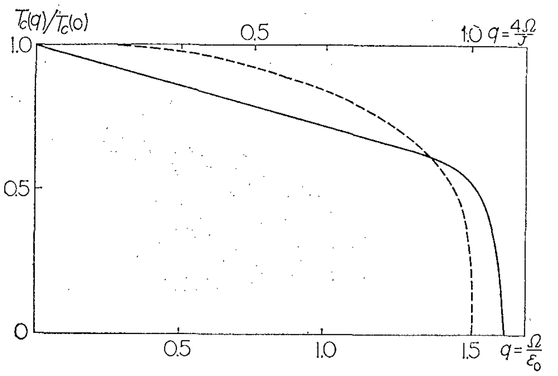

Fig. 6. Isotope effect of the critical temperature in the cluster approximation for the case $\varepsilon_1 \fallingdotseq 5\varepsilon_0$. Dashed line shows the molecular field approximation.

It would be interesting to examine theoretically the variation of T_c in the mixed crystal $KH_{2(1-x)}D_{2x}PO_4$ with the degree of deuteration x. In the simplest approximation, we may assume

$$\Omega = (1-x)\Omega_H + x\Omega_D \text{ or}$$
$$q = (1-x)q_H + xq_D. \qquad (4\cdot19)$$

Then using the result given in Fig. 6, we can evaluate T_c for the mixed crystal when the ratio $p=q_D/q_H$ is fixed. In Fig. 7 the calculated ratios $T_c(x)/T_c(1)$ for several p values are shown together with the experimental values observed in a recent experiment by Kaminow.[18] Agreement between the theory and experiment is fairly satisfactory in view of the comparatively large experimental error. It should be noted that if we adopted the molecular field approximation, the theory would predict an x-dependence of $T_c(x)$ far from the linear relation, as shown in Fig. 7. Thus the cluster approximation removes some of the defects involved in the molecular field approximation described above, but it cannot remove the difficulties encountered before in explaining the absence of isotope effects on the Curie constant and saturated polarization.

Some of the difficulties mentioned above, however, may be overcome by considering the degree of freedom of the ionic displacements which are assumed to be responsible for the electric polarization. Therefore let us take the Hamiltonian (2·20) and see what comes out when the molecular field approximation is applied to it. Neglecting small terms which involve K_{ij} and L_{ij}^n, we rewrite

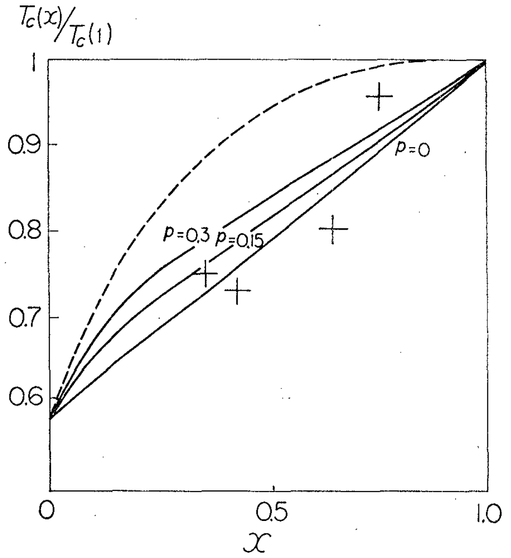

Fig. 7. Theoretical critical temperature $T_c(x)$ of a partially deuterated crystal as a function of the degree of deuteration x. Dashed line shows the result based on the molecular field approximation. Experimental values are shown by +.

(2·20) as

$$H = -(\mu^2/2)\sum_{n\,n'} \sigma_n G_{n\,n'} \sigma_{n'} - \mu E \sum_n \sigma_n - 2\Omega \sum_i X_i - (1/2)\sum_{ij} J_{ij} Z_i Z_j - \sum_{ni} v_{ni}\, \sigma_n Z_i. \qquad (4\cdot20)$$

In the molecular field approximation, the Hamiltonian per proton is given by

$$H_{\text{proton}} = -J\bar{Z}\cdot Z - v\bar{\sigma}\cdot Z - 2\Omega X \equiv -fZ - 2\Omega X \qquad (4\cdot21)$$

and that for one dipole by

$$H_{\text{dipole}} = -[\mu E + \mu^2 G\bar{\sigma} + v\bar{Z}]\sigma, \qquad (4\cdot22)$$

where J and $\bar{Z}$ are the same as before while v and G are defined respectively by

$$v = \sum_n v_{ni} = \sum_i v_{ni}$$

and

$$G = \sum_{n'} G_{n\,n'}\,. \qquad (4\cdot23)$$

$\bar{Z}$ should be determined self-consistently by an aquation

$$\bar{Z} = \mathrm{Tr}[Z\exp(-\beta H_{\text{proton}})]/\mathrm{Tr}[\exp(-\beta H_{\text{proton}})] = \frac{(J\bar{Z}+v\bar{\sigma})\tanh[\beta\sqrt{(J\bar{Z}+v\bar{\sigma})^2+4\Omega^2}/2]}{2[(J\bar{Z}+v\bar{\sigma})^2+4\Omega^2]^{1/2}}, \qquad (4\cdot24)$$

and similarly $\bar{\sigma}$ should be the solution of an equation

$$\bar{\sigma} = \mathrm{Tr}[\sigma\exp(-\beta H_{\text{dipole}})]/\mathrm{Tr}[\exp(-\beta H_{\text{dipole}})] = \tanh[\beta(\mu E + v\bar{Z} + \mu^2 G\bar{\sigma})]\,. \qquad (4\cdot25)$$

By our assumption, the electric polarization may be put equal to

$$P = N\mu\,\bar{\sigma}\,, \qquad (4\cdot26)$$

and by solving the simultaneous equations (4·24) and (4·25), we can easily obtain the spontaneous polarization P_s below the critical temperature T_c and susceptibility χ above and below T_c. Here we shall present only the result for the susceptibility above T_c:

$$\chi = \frac{(N\mu^2/k)}{T - \left(\dfrac{\mu^2 G}{k} + \dfrac{v^2}{kJ}\cdot\dfrac{\tanh(\beta\Omega)}{q-\tanh(\beta\Omega)}\right)}\,. \qquad (4\cdot27)$$

The critical temperature T_c is the temperature at which χ tends to infinity and both $\bar{Z}$ and $\bar{\sigma}$ become zero. From (4·27) it is given by

$$kT_c=\mu^2G+v^2\tanh(\Omega/kT_c)/J[q-\tanh(\Omega/kT_c)] \tag{4·28}$$

which may also be written as

$$1+\frac{v^2}{J(kT_c-\mu^2G)}=q/\tanh(\Omega/kT_c)\ . \tag{4·29}$$

In the limit $v=0$, (4·29) reduces to (4·7) as it should. Since $\bar{\sigma}$ tends to unity as T goes to zero, the maximum polarization P_M is in the present model

$$P_M=N\mu\ . \tag{4·30}$$

Thus there appears no isotope effect in P_M, although the critical temperature calculated from (4·29) depends sensitively on Ω.

§ 5. Summary and discussion

In the previous sections we have discussed a model of KDP which includes the Slater model in one limit and the Blinc model as another limit. The large isotope effect observed on the critical temperature of this substance is explained, following Blinc, by taking into account the tunneling motion of protons. A conclusion inherent to a theory of the Blinc type is that the spontaneous polarization cannot attain its maximum value even at the absolute zero of temperature because of the presence of the tunneling motion. This result may be in accord with the electro-optical observations of Zwicker and Scherrer,[10] but the recent measurement of the dielectric constant by Mayer et al.[8] seems to support rather the result of Bantle's experiment[9] which reveals no isotope effect on the spontaneous polarization. If there is little difference in the saturated polarization between KH_2PO_4 and KD_2PO_4, the Blinc model has to be modified in such a way that the main part of the dielectric polarization is contributed by the ionic displacements and that the ordering in the proton system merely plays the role of a trigger to make the ionic lattice polarize spontaneously.

At present there seems to exist no conclusive evidence as to whether or not the protons are really carrying out tunneling motions. From the theoretical side, it is difficult to draw any definite conclusion on this point, so long as we are concerned only with the equilibrium properties of KDP as in this paper. In our theory, the presence of the tunneling motion is characterized by a parameter $q=\Omega/\varepsilon_0$. From the discussion of the isotope effect on T_c, we have deduced a theoretical value $q=1.4$ for KH_2PO_4. On the other hand, as is easily shown, 2Ω is equal to the energy splitting of the vibrational ground state of a proton caused by tunneling motion. According to Hadzi's experiment on far infrared absorption,[15] this energy separation may be identified with the energy of an observed photon

$$2\Omega = 123\ \mathrm{cm}^{-1}.$$

If we assume that there exists no tunneling motion in KD_2PO_4, (Hadzi could not observe the corresponding photon in KD_2PO_4.) then ε_0 is related to the critical temperature of KD_2PO_4 $T_c^D = 213$ °K, on using the cluster approximation with $n=5$, by the relation

$$kT_c^D = 1.39\ \varepsilon_0,$$

from which we have $\varepsilon_0 = 105\ \mathrm{cm}^{-1}$ and hence $q = 0.56$. This q value is somewhat smaller than the theoretical value, although the order of magnitude is the same. The observations on the critical temperatures of partially deuterated KDP are not inconsistent with the present theory. From these results, therefore, it is difficult to make a definite choice of models. The tunneling motion of the protons, if it ever exists, will be more closely connected with the dynamical properties of the crystal such as the inelastic scattering of neutrons and dielectric relaxation. We shall discuss such subjects in the second part of this paper.

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