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ON THE SELF-CONSISTENT FIELD APPROACH TO HYDROGEN-BONDED PHASE TRANSITIONS

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Abstract: A numerical analysis using the self-consistent molecular field equations is performed in order to test the validity of the tunneling model in KN_2PO_4 and KD_2PO_4. On observing the presented numerical data we confirm a nice agreement with the tunneling model in contradiction with the central mode-type Debye dispersion as recently proposed.

1. Introduction

Many critical phenomena including those experienced by hydrogen-bonded ferroelectrics (KH_2PO_4 and similar substances), nematic liquid crystals, or even certain ferromagnetic compounds (e. g. invar) might well be described using the same pseudo-spin formalism which is represented by the Ising model with a transverse field (also named the »tunneling« model). Essential features of the model are established by two physical sources, one being the classical potential energy coming either from long-range dipole-dipole forces or short-range exchange interactions, as in all Ising ferromagnets, while the other physical source being a neat quantum-mechanical »transverse« field. This field comes from an average lattice potential which is responsible for the motion of given ions. In each case it has a different nature as for the relevant physical meaning. It is the proton or deuteron kinetic energy as those particles change the equilibrium positions under the influence of massive phosphate groups, or it is the energy difference corresponding to neighbor dipole positions of lengthy rod-like molecules in a nematic liquid crystal, and so on.

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2. *Interactions*

The Ising model with a transverse field, for the one-half pseudo-spins, on N lattice sites, is given by

$$- H = 2\Omega \sum_{j=1}^{N} S_j^x + \sum_{j,k-1}^{N} (K_{jk}\, S_j^x\, S_k^x + J_{jk}\, S_j^z\, S_k^z), \tag{1}$$

where the pseudo-spin variables S_j^x and S_j^z are represented by the ordinary Pauli matrices, 2Ω is the magnitude of the transverse field, to be identified with the proton (deuteron) kinetic energy, whereas K_{jk} and J_{jk} designate certain field coupling constants connecting nearest neighbor atomic sites, to be identified with effective dipole-dipole interactions. Specifically, we shall direct our further analysis to the ferroelectric-paraelectric phase transition in a hydrogen-bonded substance.

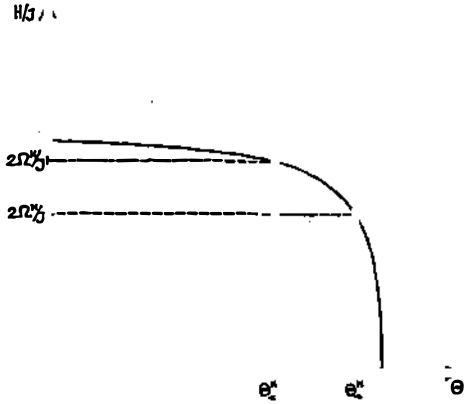

FIG.1

Fig. 1. Illustration for the isotope effect: A greater transverse field, $2\Omega^H > 2\Omega^M$, is associated with a lover reduced transition temperature, $\Theta_C^H < \Theta_C^M$.

Theories are developed recently in a number of papers or monographies[1-8], all based on the tunneling model, in order to explain the observed dynamic characteristics, in particular, the molecular field, mass-dependent transition temperature, long-range order parameter in the ordered phase and, finally, the Cochran soft ferroelectric mode in the disordered phase. However, a central mode-type Debye dispersion is also introduced in the current literature[9-12], as oposed to the soft ferroelectric mode. Since the problem in our view is very important we have calculated a number of dynamical characteristics of KH_2PO_4 with isotope impurities in order to test the tunneling model as precisely as possible.

3. *Self-consistent field equations*

The magnitude of the self-consistent molecular field H is a temperature-dependent quantity, as demonstratet in[8]. Here we take

$$H = \mathcal{J}\sqrt{(1-\Theta^2)}, \tag{2}$$

where $\mathcal{J}$ designates the effective coupling constant for which a careful analysis based on spectroscopic data shows to be almost a mass-independent quantity, whereas for Θ we take

$$\Theta = 2k\,T/\mathcal{J}. \tag{3}$$

Exactly at the transition temperature $T=T_c$, the molecular field, if the tunneling model is adapted, becomes equal to the tunneling energy 2Ω[*],

$$H(T=T_c) = 2\Omega^H. \tag{4}$$

Also we have

$$\Theta^2(T=T_c) = 1 - B^2, \tag{5}$$

where

$$B = 2\Omega^H/\mathcal{J}, \tag{6}$$

$$T_C^H = \frac{\mathcal{J}}{2k}\sqrt{(1-B^2)} \tag{7a}$$

or equivalently

$$\mathcal{J} = \frac{2k\,T_C^H}{\sqrt{1-B^2}}. \tag{7b}$$

This equation has been used to fit the parameter B.

For a mixed crystal, with c designating the concentration of deuterium bonds relative to hydrogen bonds, we assume that the field coupling constant which connects nearest neighbor atomic sites is mass-independent

$$\mathcal{J}^M = \mathcal{J}^H. \tag{8}$$

Furthermore the tunneling energy of the mixed crystal is governed by a linear law, owing to the conservation of energy

$$2\Omega^M = 2\Omega^H(1-c) + 2\Omega^D \cdot c, \tag{9}$$

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[*] The upper suffix H, or D, or M, will be respectively used to designate the quantity corresponding to KN_2PO_4, or KD_2PO_4, or a mixture of both crystals.

Table 1

SELF-CONSISTENT FIELD QUANTITIES FOR KH_2PO_4 (DESIGNATED BY H) AND KD_2PO_4 (DESIGNATED BY D)

	$2\Omega^H$ (cm^{-1})	$\mathcal{J}^H$ (cm^{-1})	$\frac{2\Omega^H}{\mathcal{J}^H}$	$\frac{2\Omega^D}{2\Omega^H}$	$2\Omega^D$ (cm^{-1})	$\frac{2\Omega^D}{\mathcal{J}^D}$
EXPTL	345	348.425	0.897	0.658	226.885	0.590
THEOR	361	398.846	0.905	0.694	250.545	0.628

Table 2

SELF-CONSISTENT FIELD TRANSITION TEMPERATURES FOR VARIOUS MIXTURE CONCENTRATIONS

c	T_C^M/T_C^H(LIN)	T_C^M/T_C^H(EXPTL)	$\delta\%$ (EXPTL)	T_C^M/T_C^H(THEOR)	$\delta\%$ (THEOR)
0.10	1.083	1.131	4.407	1.128	4.183
0.20	1.166	1.244	6.685	1.240	6.349
0.30	1.249	1.344	7.612	1.339	7.231
0.40	1.332	1.434	7.648	1.429	7.265
0.50	1.415	1.515	7.079	1.510	6.723
0.60	1.498	1.589	6.093	1.585	5.785
0.70	1.581	1.657	4.816	1.653	4.572
0.80	1.664	1.720	3.336	1.717	3.166
0.90	1.747	1.777	1.716	1.775	1.628

Note:

$$\delta\% \,(\text{EXPTL}) = \frac{T_C^M(\text{EXPTL}) - T_C^M(\text{LIN})}{T_C^M(\text{LIN})} \cdot 100$$

$$\delta\% \,(\text{THEOR}) = \frac{T_C^M(\text{THEOR}) - T_C^M(\text{LIN})}{T_C^M(\text{LIN})} \cdot 100$$

so we can write the transition temperature for a mixed crystal, T_C^M, as follows

$$T_C^M = \frac{\mathcal{J}}{2k}\{1 - B^2[1 + (P - 1)c]^2\}^{1/2}. \tag{10}$$

Here P designates the ratio of the relevant tunneling energies

$$P = \frac{2\Omega^D}{2\Omega^H}. \tag{11}$$

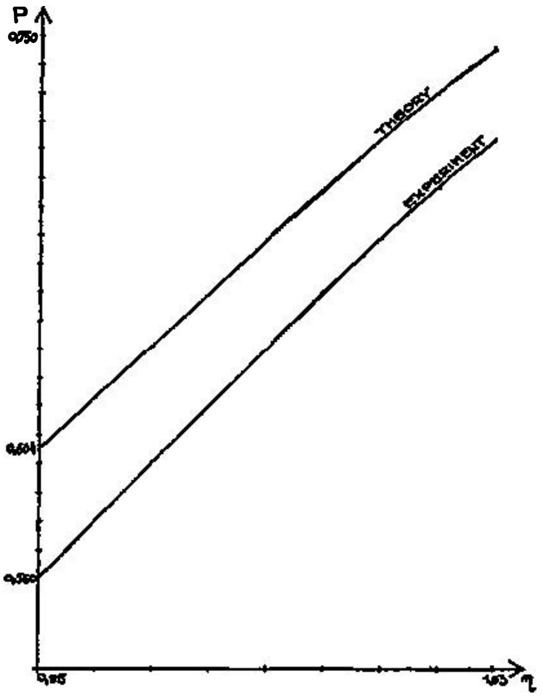

Fig. 2. The parametar P, defined by equations (11) and (14), is plotted against the parameter η, defined by Equ. (15). The latter parameter, if the lattice remains strictly unaltered when protons are replaced by deuterons, is expected to have the value $\eta = 1.00$, but is allowed to vary between 0.95 and 1.03 in steps $\Delta\eta = 0.01$. The upper curve, looking almost like a straight line, corresponds to the value $2\Omega^H = 361\ \mathrm{cm}^{-1}$ («theoretical» value[13]), whereas the lower curve, also looking almost like a straight line, corresponds to the value $2\Omega^H = 345\ \mathrm{cm}^{-1}$ («experimental« value, see Ref[14]).

The transition temperature ratio for a mixed crystal to the hydrogen-bonded crystal is given by

$$\frac{T_C^M}{T_C^H} = \left\{\frac{1 - B^2\,[1 + (P - 1)\,c]^2}{1 - B^2}\right\}^{1/2}. \tag{12}$$

For $c = 1$ we obtain the transition temperature ratio as follows

$$\frac{T_C^D}{T_C^H} = \left\{\frac{1 - (BP)^2}{1 - B^2}\right\}^{1/2}, \tag{13}$$

whereas the observed value is 223°K/122°K = 1.83. It followvs from Equ. (13)

$$P = \frac{1}{B}\,[1 + (1.83)^2\,(B^2 - 1)]^{1/2}. \tag{14}$$

This equation has been used to fit the parameter P.

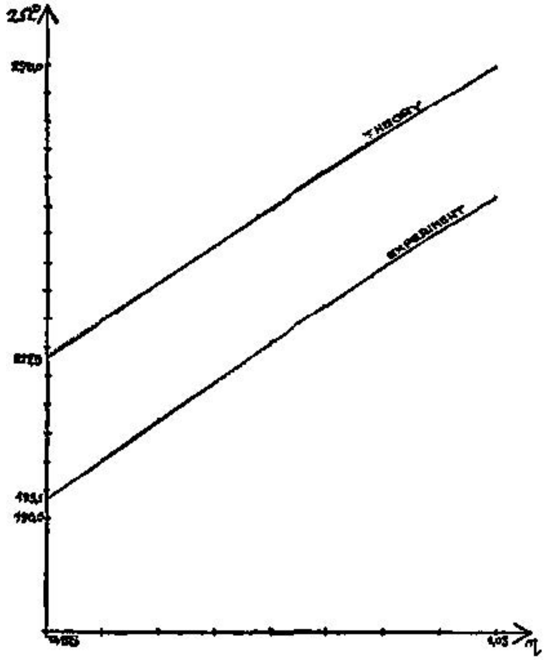

Fig. 3. Deuteron tunneling energy, $2\Omega^D$, expressed in units cm^{-1}, is plotted against the parameter η, defined by Equ. (15). This parameter is varied in the same manner as on Fig. 2. The upper and lower curves, looking almost like straight lines, correspond to the same values of $2\Omega^H$ as those on Fig. 2.

The presented numerical results, using a CDC computer, are illustrated in Fig. 1, Tables 1 and 2. Here the effective tunneling energy may be identified either with the single-particle low-lying energy difference across a double-minimum potential field[13)], or with the single-particle strong line difference as observed by a laser-excited Raman spectrum (Kaminow et al.[14)]). In fitting the self-consistent field equations we have taken both the experimentally observed value $2\Omega^H = 345$ cm^{-1}, and the theoretical value $2\Omega^H = 361$ cm^{-1}.

To see possible variations of the quantities P form Equ. (11) and deuteron tunneling energy $2\Omega^H$ on the effective coupling ratio

$$\eta = \frac{J^D}{J^H}, \tag{15}$$

we have also computed P and $2\Omega^D$ by varying η from 0.95 up to 1.03 in steps $\Delta\eta = 0.01$. The numerical results are presented in Figs. 2 and 3.

4. Conclusions

On observing the listed results one obviously comes to the conclusion that the present numerical data are fairly well in agreement with the introduced tunneling model, which requires

$$\frac{2\Omega^D}{2\Omega^H} = \frac{\sqrt{2}}{2} \cong 0.70, \tag{16}$$

whereas the data are in a sharp disagreement wiht the central mode-type Debye dispersion model (as oposed to the tunneling model), which would require

$$\frac{2\Omega^D}{2\Omega^H} \cong = 0. \tag{17}$$

Nevertheless, the present conclusion might be confirmed only by measuring the dynamic characteristics of a mixed crystal for various values of the mixture concentration, *c*, as predicted in Figs 1—3, Tables 1 and 2. Our results are also in agreement with those reported recently by Holakovsky$^{11)}$.

A more comprehensive report along the described lines is in progress.

Several excellent review articles and research papers$^{16-19)}$ on a similar subject came to our attention after the present manuscript was completed and submitted for publication. To connect the current analysis with our own conclusions we will bring here a brief summary from them all.

Measurements of the pressure and temperature dependences of the soft-mode Raman spectra in KH_2PO_4 both in the paraelectric and ferroelectric phases have been reported in $^{16)}$. Before the pressure measurements serious questions had been arisen over the nature of the soft-mode dynamics. On the one side the soft mode should be considered as a propagating excitation, whereas on the other side the soft mode also might be viewed as a single particle relaxational excitation. The reported pressure measurements$^{11)}$ demonstrate that the mode becomes underdamped at modest pressures and therefore it must be considered as a collective excitation, with the propagating nature, in good agreement with our self-consistent field approach.

The dynamics of isotopically disordered ferroelectric crystals with hydrogen bonding is considered on the basis of the coupled proton-deuteron tunneling-lattice optic-mode model in$^{17,18)}$. The theory allows us to estimate various dynamical characteristics and provides a strong support for the proton tunneling picture of ferroelectric crystals with hydrogen bonding. In conclusion the authors emphasize the importance of studying mixed crystals which become an excellent check on the different model theories applied to the KH_2PO_4 order-disorder type of ferroelcctric crystals. The conclusion in the present paper agrees fairly well with the detailed numerical analysis of $^{17,18)}$.

A two-component Ising model with a transverse field in terms of random variables is treated in$^{19)}$. The paper is primarily devoted to the polarized phase where the fluctuating longitudinal component of the molecular field is replaced by two components, one for each sublattice, to be determined by a self-consistent procedure. Numerical results are performed for various values of the average transverse field and for the transverse field disorder.

The latter parameter is defined by

$$\delta = (\Omega_A - \Omega_B) / (\Omega_A + \Omega_B),$$

where A and B designate two sublattices. For $\delta < 0.3$ the average transverse field is only weakly dependent on the concentration in[19], which fits nicely with the present analysis.

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O PRILAZU SAMOSAGLASNOG POLJA K FAZNIM PRELAZIMA S VODONIČNOM VEZOM

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Sadržaj

U radu je sprovedena analiza valjanosti tumačenja nekih dinamičkih karakteristika kristala sa vodoničnom vezom kao što su KN_2PO_4 i KD_2PO_4 na osnovu modela probijanja potencijalne barijere (»tunnerling« model). Upotrebljene su jednačine samosaglasnog molekularnog polja. Analiza je prirodno proširena i na mešane kristale uvođenjem parametra c koji označuje koncentraciju deuterijumskih veza u odnosu na vodonične veze.

Prikazani numerički podaci slažu se sa modelom probijanja potrencijalne barijere i nalaze se u kontradikciji sa Debyeevim disperzionim modelom (»central mode-type Debye dispersion« model) kako je nedavno predložen u tekućoj stručnoj literaturi. Pa ipak bi ovaj zaključak trebalo detaljno ispitati mjerenjem dinamičkih karakteristika mešanog kristala za različite vrednosti koncentracije c. Radi predviđajna teorijskih zaključaka za sada su autorima prirodno stajala na raspoloženju samo merenja spektralnih linija dvaju monokristala a to su čisti KH_2PO_4, gde je koncentracija $c = 0$, i čisti KD_2PO_4, gde je koncentracija $c = 1$. Međutim, procena efekta probijanja potencijalne barijere provedena je i za intermedijarne kristalne strukture, ukoliko bi ove i dalje egzistirale sa gledišta stabilnosti rešetke, u koracima $\Delta c = 0{,}1$.

Na osnovu jednačina samosaglasnog molekularnog polja dobija se približno linearan zakon za temperaturu prelaza jedne intermedijarne kristalne strukture. Ovaj zaključak ukazuje na vrlo prost eksperimentalni put testiranja postojećih modela. Treba napomenuti da linearni zakon ne bi trebalo očekivati na osnovu Debyeevog disperzionog modela čak ako bi i uspeo proračun temperature prelaza intermedijarnih kristalnih struktura.