ON THE AGREEMENT OF THEORETICAL AND EXSPERIMENTAL RESULTS FOR KDP FERROELECTRICS

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Abstract

The consistency of various pseudospin-phonon models with a number of apparantly disagreeable experiments are analyzed, with the purpose to confirm positive results of the theory and experiment, to explain disagreements and to point out the problems and some new phenomena which need a complete theoretical as well as a precise experimental research.

The qualitative and quantitative agreeement of the pseudospin model as associated with the tunnelling proton within the hydrogen bonds[1,2], *including its generalization towards the mixed tunnelling - pseudospin - phonon (heavy ions - K, P, O) model Hamiltonians*[3,4] *(all notatins as in Refs. 3,5)*,

$$H = 2\Omega \sum_{ir} S^x_{ir} - \sum_{ij\,rr'} J^{rr'}_{ij} S^z_{ir} S^z_{jr'} - \sum_{ijra} S^z_{ir} A^{ra}_{ij} U_{j\alpha}, \quad (1)$$

with experimental results obtained by various techniques (IR, RS, NS and NMR mostly) is the predominant subject of the present analysis. The theoretical results of Villain-author[3] *and Kobayashi*[4] *(VSK) about a qualitative behaviour of the ferreelectric mode is completed by a quantitative extimation (T.1) of basic mode parameters:*

$$w_k^2(T) = \tilde{P}|T - T_c| + Qk^2, \quad \tilde{P} = \begin{cases} P, & T > T_c \\ 2P, & T < T_c \end{cases} \quad (2)$$

$$P = \frac{K_B}{2} (2\Omega)^2 / \{J_o + J_o' \left[1 + \left(\frac{2\Omega}{\lambda_o}\right)^2\right]\} \quad (3)$$

$$Q = \frac{(2\Omega)}{J_o} \left(\frac{J_o}{g} a^2 + \frac{2J_o'}{g'} a'^2\right); \quad J_o' = \frac{1}{2m_o} \left|\frac{A_o}{\lambda_o}\right|^2,$$

$$\bar{J}_o = J_o + J_o' .$$

T.1. Theoretical predictions[3,5]

CRISTAL	2Ω	$\bar{J}_o$	J_o'	$2\Omega/\bar{J}_o$	P	$Q \cdot 10^4$
KH_2PO_4	323	328,60	63	0,98	68	9,26
KD_2PO_4	229	328,60	63	0,70	34	4,63

(2Ω, $\bar{J}_o$, J_o' in sm^{-1}, P in $cm^{-2}\,^oK^{-1}$ and Q in $cm^{-1}\,\mathring{A}^2$)

This enables a straightforward test for the physical basis of the generalized model itself as well as the total set of theoretical results following from it. For the same subject and at the same time were analyzed the results of other authors as based on the VSK model or based on recent similar models[6-8].

Having in mind the importance of the isotope effect (the replacement of H by D) as a possible test of the validity of existing theoretical models, this problem is particulary and originally elaborated. Apart from a series of original comments and auxiliary details in a widely conceived analysis we stated here only the theoretical isotopic ratios for the critical temperature (T_c), Curie constant (C) saturation polarization (P_S) and soft mode parameters (P,Q).

$$T_c^D/T_c^H = \frac{arthq}{arth(pq)} \cdot \frac{py+arth\,(pq)}{y+arthq} \simeq 1,595$$

$$C^D/C^H \simeq (l_D/l_H)^2 = 1,44$$

$$P_S^D/P_S^H \simeq lD/lH = 1,20 \qquad (4)$$

$$P_H/P_D = Q_H/Q_D = 2$$

$$(q = 2\Omega/(J_o + J_o'),\ P = \Omega_D/\Omega_H,\ y = \frac{\Omega H}{2m}\left|\frac{A_o}{\lambda_o}\right|^2$$

$$l_H = 0,35\ \mathring{A} \qquad l_D = 0,42\ \mathring{A}$$

The above estimations are nearly in the excellent agreement with experimental results[9-11] (see, also T.2).

T.2. The energy and soft mode parameters as identified (directly or indirectly) from various experiments

EXP. TECH.	2Ω	$\bar{J}_o$ (B)	P	Q
$(NS)_{inc}$	~330*	~400*	-	-

$(NS)_{coh}$	-	320**	44**	20*
RS	~340+	~350++	48,50++	-
IR	~350x	~400x	-	-

(After: Stiller et al.(*), Paul et al.(**), Kaminow et al. (+), She - Broberg (++) Palah et al.(x) (units like in T.1).

It is worthwhile to note that the dynamical model of Novaković[8], with its extension[12], is also in quite a good agreement with a wide experimental evidence. But it fails in predicting the isotope effect ratio of the soft mode parameters (probably due to inaccurate relations hetween model parameters).

Since the neutron diffraction is one of the most suitable method to test the majority of theoretical results a special attention is paid to all kinds of NS (both coherent and incoherent; also elastic, quasielastic and inelastic).

In all differential cross sections (intensities), a predominant role has the characteristic "interference effect" by Stiller[13] and the author[14], which turns out to be a direct consequence of the proton tunnelling around its equilibrium positions on the hydrogen bond. By this effect,in connection with the characteristic behavionr of the ferroelectric (soft) mode in the critical region, a long time after the famous measurements of Bacon and Pease[15], the proton tunnelling was definitely established[16] and so was the cooperative atomic displacements according to the VSK model and its visual schemitic representation[17]. The most important experiments among those mentioned (IR[18-19], RS[20-23], BS[24] and partially NMR[25], NQR[26], and EPR[27]) are analized in all aspects having included the mode analysis of Shur by group theoretical methods[28] (B_2, A_1, E and modes of other symmetries) (T.2).

As to gratify, in the recent extraordinary monograph of Blinc and Žekš[29], jointly with the monograph of Novaković[30], the greater part of the present subject has been elucidated for a wide class of KDP isomorphas. According to their analysis, the NMR, NQR and EPR experiments are by all means consisted with the tunneling - pseudospin-phonon model. Neverthelless, a quantitative tests toward such a model are lacking as yet.

To conclude it should be emphasized that various concepts of the pseudospin models in contex to a number of apparantly disagreeable experiments is discussed with the purpose to confirm positive results of the theory and experiment, to explain disagreements, and to point out the problems and several new phenomena appeling for a complete theoretical (a need for a unified theory of ferroelectricty[31,32]; D_g - vibrations, to improve cross sections consistently to eminent models[33]; problems of universality and of central peaks[34]) as well as a precise experimental research (NS at small angles to "extract"[35] the "hidden informations" and, contrary, at larger values of momentum transfer[36] - to distinguish tunnelling from vibrating, etc.).

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References:1.P.G.de Gennes,Solid St.Comm.1,132,1963;2.M.Tokunaga,T.Matsubara,Progr.Theor.Phys.35,581,1966;3.J.Villain,S.Stamenković,phys.st.sol.15,585,1966;4.K.K.Kobayashi,J.Phys.Soc. Japan 24,497,1967;5.S.Stamenković,Dynamical Theory of Collective Atomic Motions in Hydrogen-Bonded Ferroelectrics,Thesis,Fac. of Nat.Scien.and Math.,Belgrade 1975/in Serbian/;6.I.V.Stasyuk, R.R.Levitskii,UFZh 14,110,1969;15,460,1970;7.J.Villain,S.Aubry, phys.st.sol.33,337,1969;8.L.Novaković,J.Phys.Chem.Solids,31,431, 1970;9.W.Bantle,Helv.Phys.Acta 15,373,1942;10.B.Zwicker,Scherrer,Helv.Phys.Acta 17,346,1944;11.J.Azoulay et all.,J.Phys.Chem. Solids 29,843,1968;12.L.Novaković,S.Stamenković,A.Vlahov,J.Phys. Chem.Solids 32,487,1971;13.H.Stiller,Ber.Bunsenges.Phys.Chem.72, 94,1968;14.S.Stamenković,FTT 10,861,1968;15.G.Bacon,R.Pease, Proc.Roy.Soc. A230,359;16.Th.Plesser,H.Stiller,Solid St.Comm. 7,323,1969;H.Grimm,H.Stiller,Th.Plesser,phys.st.sol. 42,207, 1969;17.W.Cochran,Adv.Phys. 10,401,1961;18.I.Pelah,E.Wiener,J. Chem.Phys. 43,2332,1965;19.Y.Sato,Y.Machida,Solid St.Comm. 7, 327,1969;20.I.P.Kaminow,T.C.Damen,Phys.Rev.Lett. 20,1105,1968; 21.D.K.Agrawal,C.H.Perry,in:Light Scatt.Solids,ed.M.Balkanski, Flammarion,Paris 1971;22. C.Y.She,T.W.Broberg,D.F.Edwards,Phys. Rev./B/ 4,1580,1971;23.R.Blinc,B.Lavrenčić et al. phys.st.sol. /b/ 60,255,1973;24.E.M.Brody,H.Z.Cummins,Phys.Rev.Lett. 21,1263, 1968;25.R.Blinc et al.,J.Chem.Phys. 54,187,1971;56,3566,1972; 26.R.Blinc et al., Chem.Phys.Lett. 23,486,1973;27.R.Blinc et al.,Phys.Rev.159,411,1967;Solid.St.Comm. 6,635,1968;28.M.S.Shur, Krystalografya 11,448,1966;12,215,1967;FTT 8,57,1966;8,1267, 1966;29.R.Blinc,B.Žekš,Soft Modes in Ferroelectrics and Antiferroelectrics,Chap.8,9,North-Holland Publ.Comp.,Amsterdam 1974.

30.L.Novaković,The Pseudo-Spin Method in Magnetism and Ferroelectricity,Pergamon Press Inc.,New York 1975; 31.S.Stamenković,N.M.Plakida,V.L.Aksienov,T.Siklos,Ferroelectrics 14,655,1976;JINR,P-17-9226,1975;32.S.Stamenković et al., On the Tunnelling Concept...,in this issue;33. given in Refs.31,32;34.H.Beck,J.Phys.C:Solid St.Phys. 9,33,1976;35. V.L.Aksienov,S.Stamenković,to be publ. in JINR;36.J.Scalyo, Jr.,B.C.Frazer,G.Shirane,Phys.Rev./B/ 1,278,1970.