

## Phase Transitions in KDP-Type Crystals

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Received 18 September 2015 / Accepted 5 October 2015

**Abstract:** Curie temperature is determined by investigating the variation of order-parameter  $\langle S_q^z \rangle$  with temperature. The model Hamiltonian proposed by Blinc and Zeks has been modified by considering the lattice anharmonicities up to fourth order. The correlations appearing in the dynamical equation have been evaluated using double-time thermal retarded Green's function and Dyson's equation. The expressions for shift, width, renormalized soft mode frequency, Curie temperature, the expectation value of the proton collective mode components at site  $q$  ( $\langle S_q^z \rangle$ , and  $\langle S_q^x \rangle$ ) have been derived and discussed in KDP - type crystals. By fitting model values of physical quantities, the temperature dependence of  $\langle S_q^z \rangle$ , and  $\langle S_q^x \rangle$  for different value of four-body coupling have been calculated. The theoretical results are found in good agreement with the experimental results.

**Keywords:** Phase transition, Curie temperature, Green's function, Dyson's equation, Soft mode frequency

### Introduction

It was first shown by Bush<sup>1</sup> that potassium dihydrogen phosphate, KDP ( $\text{KH}_2\text{PO}_4$ ), exhibits a phase transition at low temperature. KDP is prototype of a family of crystals with bridging hydrogen bonds and its physical properties have been extensively studied<sup>2-13</sup>. Above the Curie temperature ( $T_c$ ), KDP has tetragonal structure belonging to space group  $I\bar{4}2d$  ( $D_{2d}^{12}$ ). The orthorhombic phase belongs to space charge group  $\text{Fdd2}$  ( $C_{2v}^{19}$ ) and exists at room temperature lower than  $T_c = 123$  K. In the ferroelectric phase the positions of all hydrogen are fixed to  $\text{PO}_4$  radicals and a spontaneous polarization appears along the  $c$ -axis, and is not attributed directly to hydrogen, but to the displacement of  $\text{K}^+$  ions and deformation of the tetrahedra of  $\text{PO}_4$  radicals which are induced by the ordered arrangement of hydrogen. In the paraelectric phase the hydrogen atoms moves between two equivalent equilibrium

positions in the O-H...O hydrogen bonds, linking the PO<sub>4</sub> tetrahedral, and the configuration of hydrogen is random and the spontaneous polarization disappears. Below T<sub>c</sub> this motion freezes out and the structure orders. This ordering is gradual and accompanied by displacement of the heavy atoms<sup>14</sup>. The real nature of the ferroelectric phase transition and the isotope effect on T<sub>c</sub> for *H* → *D* exchange in KDP-type ferroelectrics has not been fully explained<sup>14-16</sup>. The proton tunneling mode<sup>17</sup>, the earliest model used to explain the isotope effect, predicted the displacive type of phase transition. More recent crystal lattice dynamics measurements, on the other hand, have suggested the order-disorder mechanism of phase transition, an extensively discussed elsewhere<sup>15-16</sup>. Raman spectroscopic studies confirm that the ferroelectric phase transition in KDP (KH<sub>2</sub>PO<sub>4</sub>), DKDP (KD<sub>2</sub>PO<sub>4</sub>) and their mixed crystals is due to the “order-disorder dynamics” of PO<sub>4</sub> dipoles<sup>8</sup>.

Kaminow and Damen<sup>18</sup> first observed the soft mode associated with the ferroelectric phase transition of the KDP-type crystals at 122.3 K by measuring the low frequency Raman scattering in x (yx)y configuration. Since then B<sub>2</sub> (Z) soft mode, which is connected to the susceptibility along the crystalline c-axis through the Lyddane-Sachs-Teller relation<sup>19</sup>, has been extensively studied by Scott<sup>20</sup> and interpreted using the pseudo-spin model<sup>17, 21, 22</sup> and its modifications<sup>6, 23</sup>. In these theories, such a particular mode of proton motions along hydrogen bonds in a-b plane is coupled to other ion modes, bearing an electrical dipole moment along c-axis, is considered to play an essential role for the ferroelectric transition and therefore little attention has been paid to the modes other than B<sub>2</sub> (Z) soft mode. In KDP crystals, however, there are four tunneling protons in a primitive unit cell of the paraelectric phase and consequently four normal modes are belonging to a B<sub>2</sub> (Z), a doubly degenerate E(x, y) and A<sub>2</sub> modes<sup>24</sup>. The E (x, y) mode, which is both infrared and Raman active, provides valuable information, because this mode as well as B<sub>2</sub> (Z) mode, reflect the nature of collective proton motion which triggers the phase transition, and moreover, in contrast to B<sub>2</sub> (Z), it is directly related to the polarization along the crystalline a-axis.

At first, Pak<sup>25</sup> employed Green's function methods in the order-disorder type ferroelectrics, who however, did not consider the anharmonic interactions. The phonon anharmonic interactions have been found very important in explaining dielectric, thermal and scattering properties of solids by many authors<sup>9-13, 26</sup> in the past. Pak's theory was further developed by Ramakrishnan and Tanaka<sup>27</sup>, who calculated the excitation spectrum of the system, but did not consider the anharmonic interactions. Their attempt, however, established the superiority of Green's function method over the other methods. Ganguli<sup>28</sup> et al modified Ramakrishnan and Tanaka theory by considering anharmonic interaction. Their treatment explains many features of order-disorder ferroelectrics. However, due to insufficient treatment of anharmonic interactions, they could not explain quantitatively good results and could not describe some very interesting properties, like dielectric properties, acoustic attenuation, relaxation rate *etc.*

In the present study, the four- particle cluster model Hamiltonian with the phonon anharmonicity upto fourth order has been taken to theoretical study of phase transitions in KDP-type crystals, using the double time Green's function method and Dyson's equation. The proton Green's function and phonon Green's function have been solved for the collective system. Expressions for collective mode frequency shifts, widths, Curie temperature, and the expectation value of the proton collective mode components at site q ( $\langle S_q^z \rangle$  and  $\langle S_q^x \rangle$ )

have been derived and discussed in KDP-type crystals. By fitting model values of physical quantities, the temperature dependence of  $\langle S_q^z \rangle$  and  $\langle S_q^x \rangle$  for different value of four-body coupling have been calculated. The theoretical results are found in good agreement with the experimental results.

### Theory of application to cluster model Hamiltonian

For KDP crystals, the four - particle cluster model Hamiltonian<sup>14</sup> alongwith third-and fourth-order phonon anharmonic interaction terms is expressed as:

$$\begin{aligned}
 H = & -2\Omega \sum_i S_i^x - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z - \frac{1}{4} \sum_{ijkl} J'_{ijkl} S_i^z S_j^z S_k^z S_l^z \\
 & + \frac{1}{4} \omega_k (A_k^+ A_k + B_k^+ B_k) - \sum_i \bar{V}_{ik} S_i^x A_k \\
 & + \sum_{\bar{k}_1, \bar{k}_2, \bar{k}_3} V_3 (\bar{k}_1 \bar{k}_2 \bar{k}_3) A_{\bar{k}_1}^-, A_{\bar{k}_2}^-, A_{\bar{k}_3}^- \\
 & + \sum_{\bar{k}_1, \bar{k}_2, \bar{k}_3, \bar{k}_4} V_4 (\bar{k}_1 \bar{k}_2 \bar{k}_3 \bar{k}_4) A_{\bar{k}_1}^-, A_{\bar{k}_2}^-, A_{\bar{k}_3}^-, A_{\bar{k}_4}^-
 \end{aligned} \tag{1}$$

where the first two terms constitute the original pseudo spin model Hamiltonian and the third is the quadrupole contribution (the four-body interaction).  $S_i^x$  is the tunneling operator which measures the tunneling power of the proton between the hydrogen double well,  $2\Omega$  the tunneling frequency and  $S_i^z$  the half of the difference of the occupation probabilities for the proton in the two equilibrium positions of hydrogen bond.  $J_{ij}$  is the two body coupling coefficient is the same for energy pair of protons in KDP and the four body coupling coefficient  $J'_{ijkl}$  refers to the four hydrogen bonds in the  $\text{PO}_4$  group in KDP,  $\omega_k$  is bare phonon frequency:  $A_k$  and  $B_k$  are displacement and momentum operators.  $\bar{V}_{ik}$  is proton-lattice interaction term:  $V_3$  and  $V_4$  are the third- and fourth order anharmonic coefficients, defined by Maradudin *et al.*<sup>32</sup>.

### Proton Green's function:

The proton Green's function  $\langle\langle S_q^z(t); S_{q'}^z(t') \rangle\rangle$  have been evaluated for the collective motion of the system, using model Hamiltonian Equation 1. The higher order correlations in the proton's Green's function have been evaluated using the symmetrical decoupling scheme, after applying the Dyson's treatment. With this approach, one gets

$$\lim_{\varepsilon \rightarrow 0} G_{qq'}^{zz}(\omega + j\varepsilon) = \frac{\Omega \langle S_q^x \rangle \delta_{qq'}}{\pi[\omega^2 - \tilde{\Omega}^2 + j\Gamma_s(q, \omega)]} \tag{2}$$

Where  $\tilde{\Omega}$  is the proton renormalized frequency of the coupled system, which on solving self consistently takes the form

$$\tilde{\Omega}^2 = \Omega^2 + 2\Omega\Delta_s(q, \omega) \tag{3}$$

$\Delta_s(q, \omega)$  and  $\Gamma_s(q, \omega)$  represent collective proton mode frequency shift and width respectively. The collective proton mode half width, is given by

$$\Gamma_s(q, \omega) = \frac{-4\pi \bar{V}_q^2 \omega_q^2 \langle S_q^x \rangle \delta'_{qq} \Gamma_p}{\Omega[(\omega^2 - \tilde{\omega}_q^2)^2 + 4\omega_q^2 \Gamma_p^2]} + \frac{\pi bc^2}{2\tilde{\Omega}} \{\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})\} \\ + \frac{\pi a^2 \hat{\Omega}}{2b} \{\delta(\omega - \hat{\Omega}) - \delta(\omega + \hat{\Omega})\}, \quad (4)$$

The expectation value of the proton collective mode component at site 'q' have been obtained<sup>33</sup> as

$$\langle S_q^x \rangle = \frac{\Omega}{\tilde{\Omega}} \tanh\left(\frac{\beta \tilde{\Omega}}{2}\right), \quad \langle S_q^y \rangle = 0, \text{ and } \langle S_q^z \rangle = \frac{a}{2\tilde{\Omega}} \tanh\left(\frac{\beta \tilde{\Omega}}{2}\right) \quad (5)$$

where

$$\tilde{\Omega}^2 = a^2 + b^2 - bc$$

with

$$a = \sum_q J_q \langle S_q^z \rangle + \sum_{q'} J'_{q'} \langle S_{q'}^z \rangle^3; \\ b = 2\Omega;$$

$$c = \sum_q J_q \langle S_q^x \rangle + 3 \sum_{q'} J'_{q'} \langle S_{q'}^x \rangle \langle S_{q'}^z \rangle^2$$

Equation 5 represents a system of 3N equations for the average values of the collective mode components. The solution of this system will, however, be stable only if they minimize the free energy, i.e., if  $\langle S_q^z \rangle = \langle S_{q'}^y \rangle = 0$ , and

$$\text{so } \langle S_q^x \rangle = \frac{\Omega}{(4\Omega^2 - 2\Omega \sum_q J_q \langle S_q^x \rangle)^{1/2}} \tanh\left(\frac{(4\Omega^2 - 2\Omega \sum_q J_q \langle S_q^x \rangle)^{1/2}}{2k_B T}\right), \quad (5a)$$

Equation 5a, represent the paraelectric phase which exists at all temperature ( $T > T_c$ ), and in the ferroelectric phase ( $T < T_c$ )<sup>31</sup>, as

$$\langle S_q^x \rangle = \frac{2\Omega}{\sum_q J_q + \sum_{q'} J'_{q'} \langle S_{q'}^z \rangle^2}, \text{ and } \langle S_q^z \rangle = \frac{1}{2} \tanh\left(\frac{a}{2k_B T}\right) \quad (5b)$$

where  $\beta = (k_B T)^{-1}$ ,  $k_B$  is Boltzmann's constant and T the absolute temperature.

### Phonon Green's function

The acoustic mode frequency is obtained on solving phonon Green's function  $\langle\langle A_q; A_q^+ \rangle\rangle$  the higher order correlations in the phonon response have been calculated without decoupling and using renormalized Hamiltonian, as

$$\tilde{\omega}_q^2 = \tilde{\omega}_q^2 + 2 \omega_q \Delta_P(q, \omega) \quad (6)$$

with  $\tilde{\omega}_q^2 = \omega_q^2 + 8\omega_q(2V_3 + V_4)\coth\left(\frac{\beta\omega_q}{2}\right)$  calculating equation (6) self consistently and approximating, the collective mode frequency is given by

$$\tilde{\omega}_{q\pm}^2 = \frac{1}{2}(\tilde{\omega}_q^2 + \tilde{\Omega}^2) \pm \frac{1}{2}[(\tilde{\omega}_q^2 + \tilde{\Omega}^2)^2 + 16\bar{V}_q^2 \omega_q^2 \Omega \langle S_q^x \rangle]^{1/2} \quad (6a)$$

### Transition temperature

In the vicinity of transition (Curie) temperature in the paraelectric phase  $\langle S_q^z \rangle = 0$ , one may expand  $\tilde{\omega}_{q-}$  in the power of  $(T - T_c)$  around its value at  $T_c$  getting immediately

$$\tilde{\omega}_{q-}^2 = \left( \frac{\partial \tilde{\omega}_{q-}^2}{\partial T} \right)_{T=T_c} (T - T_c) \quad (7)$$

$$\tilde{\omega}_{q-}^2 \cong \gamma \times (T - T_c) \quad ; \text{ using Eq. (3)} \quad (7a)$$

$$\text{where} \quad \gamma = \frac{\Omega^2 \hat{J}}{\left[ k_B T_c^2 \cosh\left(\frac{\Omega}{k_B T_c}\right) \right]} \quad (8)$$

with effective exchange coupling constant

$$\hat{J} = J_0 + \frac{2\bar{V}_q^2 \omega_q}{\tilde{\omega}_q} \bigg|_{T=T_c} \quad (9)$$

and transition temperature

$$T_c = \Omega \left[ k_B \tanh^{-1}\left(\frac{4\Omega}{\hat{J}}\right) \right]^{-1} \quad (10)$$

### Results and Discussion

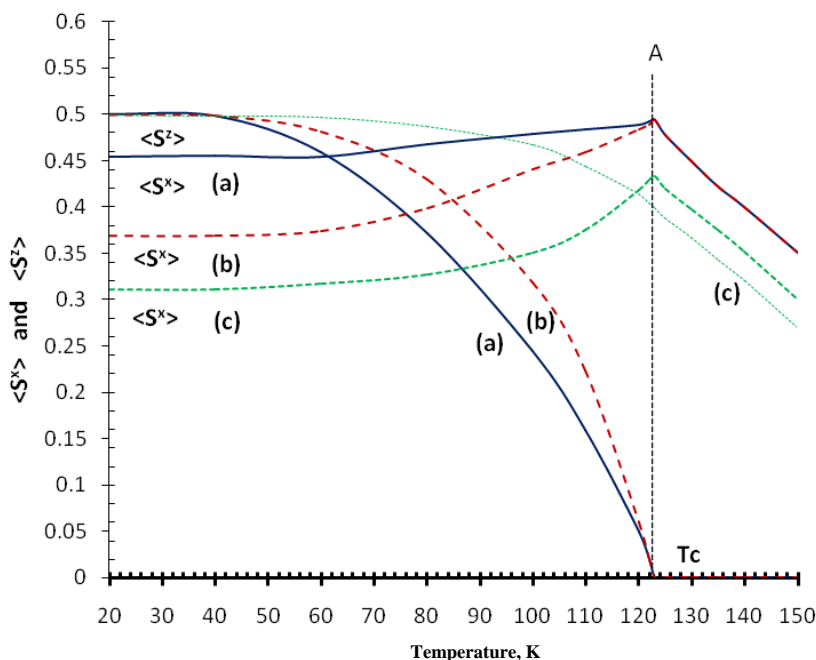
By using following model values of physical quantities given by Lyddane *et al.*<sup>19</sup>, Samara<sup>29</sup>, Chaudhuri *et al.*<sup>30</sup> and Zikai *et al.*<sup>31</sup>:

$\Omega = 82 \text{ cm}^{-1}$ ,  $J = 344 \text{ cm}^{-1}$ ,  $J' = 440 \text{ cm}^{-1}$ ,  $\bar{\nu}_{ik} = 25.56 \text{ cm}^{-1}$ ,  $\omega_k = 153 \text{ cm}^{-1}$ , and  $T_c = 123 \text{ K}$ . The temperature dependence of  $\langle S_q^z \rangle$  and  $\langle S_q^x \rangle$  have been calculated for  $\text{KH}_2\text{PO}_4$  (KDP) crystal are reported in Table 1 and shown in Figure 1.

**Table 1.** Calculated values of  $\langle S_q^z \rangle$  and  $\langle S_q^x \rangle$  for  $\text{KH}_2\text{PO}_4$  (KDP) crystal for different values of  $J'$ .

Temperature (K)	$\langle S_q^z \rangle$			$\langle S_q^x \rangle$		
	$J' = J/3$	$J' = 4J/3$	$J' = 7J/3$ Present study	$J' = J/3$	$J' = 4J/3$	$J' = 7J/3$ Present study
20	0.500	0.499	0.499	0.454	0.369	0.311
40	0.498	0.499	0.499	0.455	0.369	0.311
60	0.459	0.481	0.498	0.460	0.376	0.312
80	0.257	0.278	0.487	0.482	0.446	0.317
100	0.137	0.143	0.454	0.489	0.479	0.332
120	0.102	0.104	0.409	0.490	0.485	0.354
122	0.100	0.100	0.403	0.491	0.486	0.357
123	0.000	0.000	0.400	0.492	0.492	0.358
125	0.000	0.000	0.398	0.484	0.484	0.449
130	0.000	0.000	0.389	0.468	0.468	0.457
135	0.000	0.000	0.373	0.446	0.446	0.443
140	0.000	0.000	0.352	0.426	0.426	0.436
145	0.000	0.000	0.320	0.408	0.408	0.410
150	0.000	0.000	0.300	0.396	0.396	0.392

In Figure 1, the curve 'a' is the case of  $J' = J/3 < 4J/3$ , curve 'b' is  $J' = 4J/3 < 7J/3$ , curve 'c' is  $J' = 7J/3 > 4J/3$ . In curve 'a' and 'b' the value of  $\langle S_q^z \rangle$  increases to the saturated value 0.5 from zero, when temperature decreases from transition temperature. That is the case of second order phase transition. But in curve 'c' the change of  $\langle S_q^z \rangle$  with the temperature starts from a non-zero value  $\langle S_q^z \rangle$  at point A that is to say, when temperature decreases  $\langle S_q^z \rangle$  increases to the saturation value from the finite value of  $\langle S_q^z \rangle$ . This is the case of first order phase transition. The temperature at point 'A' is transition temperature ( $T_c$ ), and the value of  $\langle S_q^z \rangle$  at 'A' is the discontinuity of  $\langle S_q^z \rangle$ . The value of  $\langle S_q^x \rangle$  decreases when temperature decreases in the ferroelectric phase. On the other hand, in paraelectric phase the value of  $\langle S_q^x \rangle$  decreases when temperature increases from transition temperature.



**Figure 1.** Temperature dependence of  $\langle S_q^z \rangle$  and  $\langle S_q^x \rangle$  for  $\text{KH}_2\text{PO}_4$  (KDP) crystal for different values of  $J'$ . (i)  $J' = J/3$ , (ii)  $J' = 4J/3$ , and (iii)  $J' = 7J/3$  (present study).

The Green's function method and Dyson's equation treatment, using model Hamiltonian, Equation 1; for hydrogen bonded ferroelectrics give the expression for collective mode frequency shifts and widths by considering all the possible interactions. In the paraelectric phase the temperature dependence of normalized collective phonon frequency enables one to calculate the transition temperature ( $T_c$ ) Equation 10; and effective exchange coupling constant  $\hat{J}$ , Equation 9; which increases due to proton-phonon coupling and decreases due to anharmonic interactions. Thus the Green's function method with Dyson's equation treatment conveniently describes the transition properties of  $\text{KH}_2\text{PO}_4$  (KDP) - system. The theoretical results are found in good agreement with the experimental results.

#### Acknowledgement

The authors wish to thank Dr K S Bartwal RRCAT, Indore, Dr O P Thakur, DRDO, New Delhi for the valuable suggestions and encouragement.

#### References

1. Busch G, *Helv Phys Acta*, 1938, **11**, 269-298; DOI:10.5169/seals-110854
2. Mason W P, *Phys Rev.*, 1946, **69**, 173.
3. Jona F and Shirane G, *Ferroelectric Crystals*: Pergamon Press, 1962.
4. Kaminow I P and Damen T C, *Phys Rev Lett.*, 1968, **20**, 1105.
5. Tokunaga M and Matsubara T, *Prog Theor Phys.*, 1966, **35**, 581-599; DOI:10.1143/PTP.35.581
6. Kobayashi K K, *J Phys Soc Japan*, 1968, **24**(3), 497-508; DOI:10.1143/JPSJ.24.497
7. Tokunaga M, *Prog Theor Phys.*, 1984, **80**, 156-162.

8. Tominaga Y, Tokunaga M and Tatsuzaki I, *Ferroelectrics*, 1985, **63**(2), 171-178; DOI:10.1080/00150198508221398
9. Upadhyay T C and Semwal B S, *Ind J Pure Appl Phys.*, 2002, **40**, 615.
10. Upadhyay T C and Semwal B S, *Pramana J Phys.*, 2003, **60**(3), 525-533; DOI:10.1007/BF02706161
11. Upadhyay T C, Bhandari R S and Semwal B S, *Pramana J Phys.*, 2006, **67**(3), 547-552; DOI:10.1007/s12043-006-0016-y
12. Deorani S C, Naithani U C and Semwal B S, *Ind J Pure Appl Phys.*, 1999, **37**, 215.
13. Deorani S C, Singh P and Yadav M S, *Mat Sci Res India*, 2011, **8**(1), 137-147.
14. Blinc R and Zeks B, *Ferroelectrics*, 1987, **72**(1), 193-227; DOI:10.1080/00150198708017947
15. Tokunaga M and Matsubara T, *Ferroelectrics*, 1987, **72**(1), 175-191; DOI:10.1080/00150198708017946
16. Tokunaga M and Tatsuzaki I, *Phase Trans.*, 1984, **4**(2), 97-155; DOI:10.1080/01411598408220327
17. Blinc R, *J Phys Chem Solids*, 1960, **13**(3-4), 204-211; DOI:10.1016/0022-3697(60)90003-2
18. Kaminow I P and Damen T C, *Phys Rev Lett.*, 1968, **20**, 1105-1108.
19. Lyddane R H, Sachs R G and Teller E, *Phys Rev.*, 1941, **59**, 673.
20. Scott J F, *Rev Mod Phys.*, 1974, **46**, 83.
21. Tokunaga M and Matsubara T, *Prog Theor Phys.*, 1966, **35**(4), 581-599; DOI:10.1143/PTP.35.581
22. Gennes P G, *Solid State Commun.*, 1963, **1**(6), 132-137; DOI:10.1016/0038-1098(63)90212-6
23. Katiyar R S, Ryan J F and Scott J F, *Phys Rev.*, 1971, **B4**, 2635; 1971, **B4**, 2685.
24. Lavrencic B B, Levstek I, Zeks B, Blinc R and Hadzi D, *Chem Phys Lett.*, 1970, **5**(7), 441-444; DOI:10.1016/0009-2614(70)80057-4
25. Pak K N, *Phys Stat Sol.*, 1973, **B60**(1), 233-239; DOI:10.1002/pssb.2220600125
26. Panwar N S and Semwal B S, *Ind J Pure Appl Phys.*, 1990, **28**, 706.
27. Ramakrishana V and Tanaka T, *Phys Rev.*, 1977, **B16**, 422.
28. Ganguli S Nath D and Chaudhuri B K, *Phys Rev.*, 1980, **B21**, 2937.
29. Samara G A, *Ferroelectrics*, 1973, **5**(1), 25-37; DOI:10.1080/00150197308235776
30. Chaudhuri B K, Ganguli Sand Nath D, *Phys Rev.*, 1981, **B23**, 2308.
31. Zikai Q, Jinbo Z and Chunlei W, *Ferroelectrics*, 1988, **101**, 164.
32. Maradudin A A and Fein A E, *Phys Rev.*, 1962, **128**, 2589.
33. Blinc R and Zeks B, *Adv Phys.*, 1972, **21**(93), 693-757; DOI:10.1080/00018737200101348