

On the deuteration induced phase transitions in $(\text{NH}_4)_2\text{PbCl}_6$ type crystals with pseudospin-lattice coupled mode model and using statistical Green's function technique

M Karar, B K Chaudhuri*, T Purohit^a and W Haase^b

Department of Solid State Physics, I A C S, Calcutta-700 032, India

* Department of Physics, A J C Bose College, Calcutta-700 020, India

^b Institute of Physical Chemistry, Darmstadt University of Technology, Petersenstrasse 20, D-64287 Darmstadt, Germany

E-mail: ssbkc@mahendra.iacs.res.in

Abstract Deuteration induced phase transitions (DIPT) occur in some H-bonded crystals like A_2MX_6 (where $\text{A} = \text{NH}_4$, $\text{X} = \text{Cl, Br, I}$ etc. and $\text{M} = \text{Pb, Pt, Se}$ etc.) showing one or no transition in the corresponding undeuterated phase. The hydrogen bonds in $(\text{NH}_4)_2\text{PbCl}_6$ type crystals of our present investigation is rather weak and hence simple spin (pseudo-spin) like ordering of the hydrogen bonds and tunneling mechanism are not sufficient to explain the DIPT or the two successive phase transitions occurring in some deuterated system. In the present paper, using two sublattice pseudospin-lattice (phonon) coupled mode (PLCM) model, we have tried to explain the origin of single phase transition in a protonated system and a double phase transition in the corresponding deuterated system. Landau theory of phase transition also supports the concept of two phase transitions in such a system under certain conditions.

Keywords Deuteration induced phase transition, Landau theory, pseudospin model

PACS Nos. 63.20.Kr, 77.80.Bh, 81.30

1. Introduction

Crystals like A_2MX_6 (where $\text{A} = \text{NH}_4$, $\text{X} = \text{Cl, Br, I}$ and $\text{M} = \text{Pb, Pt, Te, Se, S}$ etc.) are important as they show many types of interesting phase transitions [1-14]. Raman scattering study showed that $(\text{NH}_4)_2\text{PbCl}_6$ (or NHPBC) undergone only one structural phase transition (SPT) at $T_{\text{CH1}} = 78.1\text{K}$ from cubic to tetragonal structure, whereas deuterated $(\text{ND}_4)_2\text{PbCl}_6$ (NDPBC) salt undergone two structural phase transitions from a cubic to a tetragonal structure at $T_{\text{CD1}} = 80.7\text{K}$ and then to a monoclinic or orthorhombic structure between $T_{\text{CD2}} = 34$ and 38K . Very recently ferroelectric (FE) phase transition has also been confirmed in deuterated NaOD around 159K [15] while there is no phase transition in the corresponding protonated NaOH between 6K and 300K . This type of new phase which appear in some crystals on deuteration even at atmospheric pressure is called DIPT.

DIPT is also observed in various H-bonded crystals of $\text{M}_3\text{H}(\text{XO}_4)_2$ -types (with a strong intermolecular hydrogen bond

connecting two XO_4 ions), 9-hydroxyphenalenone derivatives [16] (with strong intermolecular H-bonds) and $(\text{NH}_4)_2\text{MX}_6$ -type crystals with asymmetric H-bonds. But no acceptable explanation of such DIPT has so far been reported. Our aim in this paper is to introduce for the first time, the concept of pseudospin and to develop a model for the explanation of DIPT in $(\text{NH}_4)_2\text{PbCl}_6$ -type crystals in particular, and to find the reason why there should be more than one transitions in the corresponding deuterated system.

2. Theoretical formalism

To understand the mechanism of the DIPT transition we consider the interaction between two subsystems described by the pseudospin variables S_α ($\alpha = 1$ associated with the $(\text{NH}_4^+)/(\text{ND}_4^+)$ ions denoted by σ_1 and the PbCl_6 ions denoted by σ_2). Depending on the molecular structure, strength of pseudospin-phonon interaction etc. there may have several possibilities of transitions. Neglecting the configurational restrictions, the concept of Ising model may also be derived in a more convenient way by concentrating our attention to the two "active ions",

* Corresponding Author

taking the rest of the lattice as a 'heat bath'. The basic Hamiltonian in terms of the active normal coordinates can be written as

$$H = \sum [1/2 P_i^2 + V(Q_i)] - 1/2 \sum V_{ij} Q_i Q_j, \quad (1)$$

where P_i and Q_i are the normal coordinates corresponding to the active mode. The local potential $V(Q_i)$ may have different forms and the interaction V_{ij} may be of short range or long range nature. Using the notation of Brout [17], the orthogonalized wave function $|i, L\rangle$ and $|i, R\rangle$ with configuration localized in the up (or left) or down (or right) equilibrium sites (the order disorder behaviour), respectively, of the i -th cell (or active ion) the wave function can be written as

$$\psi = |1, \alpha_1\rangle |2, \alpha_2\rangle, \dots, |N, \alpha_n\rangle, \quad (2)$$

where α may take the values of L or R to describe the microscopic system of N unit cells. Knowing the matrix element, the effective Hamiltonian (neglecting constant terms) comes out to be

$$H = -h \sum_i X_i - \frac{1}{2} \sum_{ij} J_{ij} Z_i Z_j, \quad (3)$$

where X, Y, Z are, respectively, the $x, y,$ and z components of the pseudospin variable (S). It is to be noted that eq. (3) is the usual pseudospin Hamiltonian with

$$h = \langle i, L | 1/2 P_i^2 + V(Q_i) | i, R \rangle$$

and

$$J_{ij} = V_{ij} \langle i, R | Q_i | i, R \rangle \langle i, R | Q_j | j, R \rangle.$$

Now to write the model Hamiltonian for the $(\text{NH}_4)_2\text{PbCl}_6$ type system with two active ions, we have

$$H = -2\Gamma \sum (X_{i1} + X_{i2}) - \Delta \sum (Z_{j1} - Z_{j2}) - 2\mu E \sum (Z_{j1} + Z_{j2}) - \sum_{ij} (J_{ij} Z_{i1} Z_{j1} + J_{ij} Z_{i2} Z_{j2} + K_{ij} Z_{i1} Z_{j2}) + H_{sp}, \quad (4)$$

where μ is the dipole moment, Γ is the tunneling frequency, E is the applied field, X, Y, Z are respectively, the x, y, z components of the pseudospin variable S_α ($\alpha = 1, 2$) describing the states of the active ions in double well potential. Δ is a measure of asymmetry which is zero for symmetric double well potential and Δ is also a measure of symmetry of the crystal field.

3. Theoretical calculations

For calculating the statistical average of the pseudospin variables X, Y, Z etc. and hence the electrical susceptibilities, polarization, energy spectrum, etc. we start with the double time temperature dependent Green's function, which has the general form

$$G^{m,n}(t-t') = \langle\langle S_j^m(t) | S_j^n(t') \rangle\rangle, \quad (5)$$

where $m, n = X, Y, Z$. The Fourier transform of the above Green's function with two operators S_i^m and S_j^n yields the equation of motion

$$\begin{aligned} \epsilon \langle\langle S_i^{m,n} | S_j^{m,n} \rangle\rangle_\epsilon &= (2\pi)^{-1} \langle [S_i^{m,n}, S_j^{m,n}] \rangle \\ &+ \langle\langle [S_j^{m,n}, H] | S_j^{m,n} \rangle\rangle_\epsilon \end{aligned} \quad (6)$$

where $\langle \dots \rangle$ denotes the statistical average of the enclosed operators. By using the spectral theorem, the correlations like $\langle S_j^m S_i^n \rangle$ can be calculated from

$$\langle S_j^m S_i^n \rangle = i \lim_{\epsilon \rightarrow 0} \int_{-\infty}^{\infty} (A R / B) d\epsilon, \quad (7)$$

where $A = \langle\langle S_i^m | S_j^n \rangle\rangle_{\epsilon+i\epsilon} - \langle\langle S_i^n | S_j^m \rangle\rangle_{\epsilon-i\epsilon}$,

$$B = [\exp(\beta\epsilon - 1)] \quad \text{and} \quad R = \exp[-i\epsilon(t-t')].$$

$\beta = 1/k_B T$, k_B is the Boltzmann constant and T is the absolute temperature. Using RPA (random phase approximation) type decoupling procedure one finds

$$[L] |G\rangle = |S\rangle,$$

where $[L], |S\rangle$ and $|G\rangle$ and $(9 \times 9), (1 \times 9)$ and (1×9) matrices respectively. The energy spectrum obtained from the solution of $|L\rangle = 0$ gives $\epsilon_\alpha = 0$ and $\epsilon_\alpha^2 = (\tau_\alpha^2 + D^2)$ where

$$\tau_\alpha = 2\mu E + 2J_0 \langle Z_{\alpha-1} \rangle + K_0 \langle Z_{\alpha-2} \rangle + \Delta,$$

$$D = 2\Gamma, \quad J_0 = \sum_j J_{ij}, \quad K_0 = \sum_j K_{ij}, \quad (8)$$

$$\tau_{\alpha-1} = 2\mu E + 2J_0 \sigma_1 + K \sigma_2 + \Delta,$$

$$\tau_{\alpha=2} = 2\mu E + 2J_0 \sigma_2 + K \sigma_1 + \Delta, \quad \sigma_\alpha = \langle Z_\alpha \rangle + \langle Z_{\alpha'} \rangle$$

Eq. (8) has one solution $\sigma_1 = -\sigma_2 = \sigma$ (say) which exists in the whole range of temperatures. In the protonated phase, we have only one solution which corresponds to $\sigma_1 = \sigma_2 = 0$ giving only one phase transition.

4. Pseudospin-lattice interaction

To explain the importance of the lattice interaction in the transition mechanism of NHPBC-type crystals, we write the total Hamiltonian in eq. (1) as $H_t = H_p + H_{SP}$ where H_p is given by eq (1) and

$$\begin{aligned} H_{SP} &= \sum_{iq} V_{ij} (Z_{i1} Q_q + Z_{i2} Q_q) + \sum_q (1/2M) [P_q P_{-q} \\ &+ \omega_q^2 Q_q Q_{-q}] + \sum B_{(q_1, q_2, q_3, q_4)} Q_{q_1} Q_{q_2} Q_{q_3} Q_{q_4} \end{aligned} \quad (9)$$

+ higher order terms.

where P_q and Q_q are the normal coordinates and the conjugate momenta associated with the active vibrational modes. To study the dynamic behavior of the transition, we start with the statistical Green's function, as before, like $Q_{q,-q}^{QQ}(t-t') = \langle\langle Q_q(t) | Q_q(t') \rangle\rangle$. It should be mentioned here that all the calculations made in this paper is under MFA. The equations of motion can be represented by the matrix equation [18, 21] (in units of $\hbar = 1, M = 1, c = 1$) as

$$[G_q][\Delta] = [S_q], \quad (10)$$

where G and S are (9×9) and (1×9) matrices, respectively. The energy spectrum of the coupled spin system has the form (obtained from eq. 10).

$$\Delta = (\omega^2 - \omega_q^2)(\omega^2 - 4\Gamma\Omega - B_{1q}^2)(\omega^2 - 4\Gamma\omega - B_{2q}^2) + 8\Omega\Gamma^2 V^2 q (\langle X_1 \rangle + \langle X_2 \rangle) - 2(\omega - B_{1q}^2)\Gamma V_q^2 \langle X_1 \rangle, \quad (11)$$

$$2\Omega = 2\Gamma - J_q \langle S_{1q}^z \rangle - K_q \langle S_{2q}^z \rangle,$$

$$J_q = \sum J_{ij} \exp iq(R_i - R_j),$$

$$\bar{V}_q = (N)^{-1/2} V_q,$$

$$B'(q', T) = B_q$$

$$= (6/N') \sum A(q, -q, q', -q') [2n_{q'}(T) + 1] / \bar{w}_{q'}, \quad (12)$$

where N' is the number of unit cells in the crystals, $n_{q'}(T)$ are the phonon occupation numbers and $B'(q, T)$ is the renormalized anharmonicity parameters. Eq. (11) represents a coupled six degree equation. The two phase transitions in $(\text{ND}_4)_2\text{PbCl}_6$ at T_{CD1} and T_{CD2} can be calculated from eq. 11 using the condition $\det \Delta = 0$ as $T \rightarrow T_{CD\alpha}$ ($\alpha = 1, 2$). This gives two transitions viz

$$k_B T_{CD1} = (\eta/2) \left[\tanh^{-1} \eta^3 / 4\Gamma^2 (J'_0 + K'_0) \right]^{-1} \quad (13)$$

and

$$k_B T_{CD2} = (\eta/2) \left[\tanh^{-1} \eta^3 / 4\Gamma^2 (J'_0 + K'_0)^* \right]^{-1}, \quad (14a)$$

where $\eta^2 = [(J'_0 + K'_0) + \Delta] + 4\Gamma^2$,

$$(J'_0 + K'_0)^* = (J'_0 + K'_0) + \Delta + \bar{V}_0^2 / \omega_0^2, \quad (14b)$$

$$\omega_0^2 = \omega_0^2 + A'(q=0, T_{CD2}).$$

Eqs. (13) and (14) represent two transitions in the deuterated system at T_{CD1} (independent of pseudospin-phonon interaction term) and T_{CD2} (depending on the pseudospin-phonon interaction term including anharmonicity parameter). When the pseudospin phonon interaction term is absent or not important

these two transitions are identical and behave as one transition. This is the important result of our calculation first derived in this paper.

5. Application of Landau theory

The behaviour of phase transition can also be explained within mean field approximation using Landau theory. Using the free energy F for the system described by the Hamiltonian (eq. 9) in the MFA, f can be written as (without considering the phonon interaction term, for simplicity, which would otherwise introduce additional terms about which we shall discuss at the end of this section)

$$f = F/N = J(\sigma_1^2 + \sigma_2^2) + K\sigma_1\sigma_2 - 1/\beta \left[\ln(2 \cosh \beta/2) \{ (p_1 + q\sigma)^2 + 4\Gamma^2 \}^{1/2} \ln(2 \cosh \beta/2) \{ (p_1 - q\sigma)^2 + 4\Gamma^2 \}^{1/2} \right], \quad (15a)$$

where $p = -p_1 = \Delta$, $q = (2J_0 - K_0)$

$\beta = 1/k_B T$, k_B = Boltzmann constant and T is the absolute temperature. The free energy difference (Δf) between finite and zero polarization (or before and after the transition) is given by

$$\Delta f = f(\sigma) - f(0) = (q\sigma^2 - 1/\beta) \left[\ln(\cosh \beta/2) \{ (p_1 + q\sigma)^2 + 4\Gamma^2 \}^{1/2} / \cosh(\beta/2) (p_1 + 4\Gamma^2)^{1/2} \right] + \ln(\cosh \beta/2) \{ (p_1 + q\sigma)^2 + 4\Gamma^2 \}^{1/2} / \cosh(\beta/2) (p_1^2 + 4\Gamma^2)^{1/2}. \quad (15b)$$

Since $4\Gamma^2 \ll (p_1 + q\sigma)^2$, it is possible to expand eq. (15b) in powers of σ and comparing with

$$\Delta f = A'\sigma^2 + B'\sigma^4 + C'\sigma^6 + \dots$$

one finds

$$A' = q \left[1 - (\alpha/2) \psi^{1/2} \right] + p^2 q \left\{ (\alpha/2) \psi^{3/2} - (1 - \alpha^2) \beta/4 \psi \right\}, \quad (16)$$

where, $\alpha = \tanh(\beta\psi^{1/2}/2)$, $p_1 = -p_2 = p$, $\psi = p^2 + 4\Gamma^2$.

Therefore, for a second order phase transition, $A' = 0$ which gives rise to two possible second order transition in $(\text{NH}_4)_2\text{PbCl}_6$ viz

$$q = 0 \quad \text{for } T_{CM} \text{ (say)} \quad (17)$$

and

$$4\psi^{3/2} = 2pq\psi - p^2 q \left\{ 2\alpha - \beta\psi^{1/2} (1 - \alpha^2) \right\} \quad \text{for } T_{CH2} \text{ (say)}. \quad (18)$$

The condition (eq. 17) $q = 0$ or $2J = K$ can always occur giving rise to a single phase transition with symmetric double well potential as in the case of KDP and its deuterated form. The second condition (eq. 18) is complicated depending on tunneling energy, pseudospin-phonon interaction (as already observed earlier) *etc.* However, for $\alpha = p^2[(\alpha/\Psi) - (1 - \alpha^2)\beta/2\Psi^{1/2}]$, one of the transitions, either T_{CH1} or T_{CH2} will vanish and only one transition will occur as in $(\text{NH}_4)_2\text{PbCl}_6$ type crystals or in many H-bonded crystals like $(\text{NH}_4)_2\text{SeCl}_6$, $\text{K}_3\text{H}(\text{SeO}_4)_2$ *etc.*

Thus, with asymmetric double-well potential, one can find at least two conditions (corresponding to at T_{CH1} and T_{CH2}) for which eqs. (17) and (18) are simultaneously satisfied. One of these transitions may not even appear depending on the strength of the coupling between the active ions and/or phonons. An additional condition for a second order phase transition in NABC is $B' > 0$ which gives

$$\beta^2 q^2 / p \left\{ (1/q^2) - 1 \left\{ (5q^4 + 16q^2 - 16) / 16p^2 q^2 \right\} \tanh \beta p / 2 \right. \\ \left. - \left\{ (1 - q^2) / pq^2 \right\} \tanh(\beta p / 2) - (1/8) \tanh(\beta p / 2) \right. \\ \left. - (\beta/4) \tanh(\beta p / 2) - (\beta q^2 p / 128) - (1/4) \left\{ (1 - q^2) / pq^2 \right\} \right. \\ \left. - (\beta/4p^2 q^2) (1 - q^2) \tanh(\beta p / 2) \right\} > 0, \quad (19a)$$

where

$$\xi = \left[(\alpha/2\Psi) - \left\{ (1 - \alpha^2)\beta/\Psi \right\} + 3p^2 \left\{ (1 - \alpha^2)(\beta/2\Psi) \right. \right. \\ \left. \left. - 1/\Psi^{3/2} \right\} + p^4 \left\{ 3\beta^2/4\Psi^{3/2} \right\} (2/3)(\alpha^2 - 1) + \beta^3/16\Psi \right. \\ \left. 5\beta(1 - \alpha^2)/4\Psi^2 \right]. \quad (19b)$$

Here (eq. 19), we also notice the presence of two transitions as in the case of deuterated $(\text{NH}_4)_2\text{PbCl}_6$, Rochelle salt and some other crystals. The conditions are

$$q^4/4\Psi \geq 0 \text{ for } T_{C1} \quad (20a)$$

and

$$[\xi] \geq 0 \text{ for } T_{C2}. \quad (20b)$$

A change-over from second to first order transition is also possible in NPBC when $B' = 0$ (which is considered to be the case of low temperature transition in deuterated NDPBC at $T_{CD} = 38\text{K}$). This transition is due to the presence of strong pseudospin-phonon interaction (not purely order disorder type). Here also we notice two possibilities, one for T_{CH1} ($\beta^2 q^2 / p > 0$) and the other for T_{CH2} ($[A] > 0$) transitions. For the two transitions in the deuterated phase of $(\text{NH}_4)_2\text{PbCl}_6$ one can write

$$A' = A'''(T - T_{C1})(T - T_{C2}),$$

A' is positive if $T < T_{C1}$ or $> T_{C2}$ and negative for T between T_{C1} and T_{C2} . So one can write $\sigma = 0$, $T \leq T_{C1}$ or $T \geq T_{C2}$ and

$$\sigma = \left[-A''(T - T_{C1})(T - T_{C2}) / (2c)^{1/2} \right], \\ T_{C1} \leq T \leq T_{C2} \quad (21)$$

We should, however, mention that such a Landau approach without taking into consideration of the lattice interaction with the order parameter is an approximation one. For all structural phase transitions in solids, a more accurate and fundamental explanation of phase transition would only be possible by to consider the more complicated phonon-pseudospin interaction. Such calculation is, however, very complicated but very interesting.

6. Discussion

Considering the pseudospin-lattice interaction, we have shown theoretically that in some crystals like $(\text{NH}_4)\text{PbCl}_6$, showing only one phase transition, two phase transitions might appear in the corresponding deuterated phase (DIPT). It is seen from the derived expression of the transition temperatures that one of the transitions is independent of pseudospin-lattice (phonon) interaction term (indicating purely order disorder type behavior) while the other expression depends on the lattice (phonon) interaction (associated with the interaction of the order parameter with the lattice). This is an important finding which is considered to be new. The second transition temperature T_{CD2} in the deuterated system, depending on the lattice interaction, appears at much lower temperature $\sim 38\text{K}$ in $(\text{ND}_4)_2\text{PbCl}_6$. On the other hand, the first transition temperature T_{CD1} in the deuterated system, which represents T_{CH1} in the undeuterated system, occurs around 81K. This transition might also be lower than T_{CH1} (as in the case of the second transition in the deuterated Rochelle salt) or higher than T_{CH1} (as first transition in RS). This behavior of transition depends on the strength of the higher order-phonon interaction. The phonon dependent term in the expression for the transition temperature contains anharmonicity parameter $B'(q, T)$ which might be temperature dependent (or very small temperature dependent). So several unusual behaviour could be expected depending on the sign as well as temperature dependence of the anharmonicity parameter. For weak pseudospinphonon coupling (when $\Psi = V'_0 / \omega_0^2 = 0$), $T_{CD1} = T_{CD2} = T_{CD}$ (say) which is, of course, different from T_{CD1} or T_{CD2} . Here, only one transition would be observable. However, it was mentioned earlier that structural phase transitions in crystalline solids are always "mixed type" (neither purely order-disorder or purely displacive type) and hence a second anomaly or transition (however small it might be) should be observable with highly sensitive instrumental facilities using Raman, FTIR, ESR *etc* techniques. Recently, it has been observed that $(\text{NH}_4)_2\text{SO}_4$ showed one

more transition in the low temperature regime. Interestingly, a new transition has been observed in deuterated NaOD [15]. This new transition in NaOD could also be explained with the above model (to be discussed elsewhere). Furthermore, a reverse situation, depending on the natural selection of the crystal structure and hence the strength of electron-phonon and phonon-phonon interaction is also possible where one would observe two transitions in the protonated phase as in the case of protonated β -biphenyl, and one transition in the corresponding deuterated compound. In this case, one should consider the importance of the pseudospin-phonon interaction in the protonated (undeuterated) phase with asymmetric or symmetric double well potential. A more detailed discussion on the DIPT will be published elsewhere.

References

- [1] K Gesi *J. Phys. Soc. Jpn* **48** 886 (1980)
- [2] K Gesi *J. Phys. Soc. Jpn* **50** 3185 (1981)
- [3] U T Hochli *Ferroelectrics* **35** 17 (1981)
- [4] M Fukai, T Matsuo, H Suga and Ichikawa *Solid State Commun* **84** 545 (1992)
- [5] T Asaji, Y Kume, K Ohya and T Chuta *J. Phys. Cond. Matt* **9** 2563 (1997)
- [6] Y Kume, H Muraoka, O Yamamuro and T Matsuo *J. Chem. Phys* **108** 4090 (1998)
- [7] J R Shi, Y Kume, B Amscheidt, Y C Xu, X Wu and J Pelzl *J. Phys. Cond. Matt.* **8** 5247 (1996)
- [8] M Fukai, A Inaba, T Matsuo, H Suga and M Ichikawa *Solid State Commun* **87** 939 (1993)
- [9] J F Callanan, R D Weir and E F Westrum (Jr) *J. Chem. Thermo* **24** 1001 (1992)
- [10] J E Callanan, R D Weir and E F Westrum (Jr) *Ber. Bunsenges. Phys. Chem* **96** 85 (1992)
- [11] M Ichikawa and T Matsuo *J. Mol. Struct.* **378** 17 (1996)
- [12] M Prager, A M Raab and I Svare *J. Phys.* **C16** 181 (1983)
- [13] M Punkkinen, J E Tuohi and E E Yhnen *Chem. Phys. Lett* **36** 393 (1975)
- [14] C Dimitropoulos, J Pelzl and F Borsa *Phys. Rev* **B41** 3914 (1990)
- [15] M A White and S A Moore *J. Chem. Phys.* **85** 4629 (1986)
- [16] T Mochida, A Izuoka, T Sugawara, Y Moritomo and Y Tokura *J. Chem. Phys.* **101** 7971 (1994)
- [17] R Brout *Phase Transition* (New York: Benjamin) Ch 2 (1965)
- [18] B K Chaudhuri, T Atke, S Ganguli and H Chihara *J. Phys. Soc. Jpn* **49** 608 (1980)
- [19] F Jona and G Shtranc *Ferroelectric Crystals* (New York, Mcmillan) (1962)
- [20] G A Samara and D Sammingsen *J. Chem. Phys.* **71** 1401 (1979)
- [21] S Banerjee, D Nath and B K Chaudhuri *Phys. Rev* **B24** 6469 (1981)
- [22] R Blinc and B Zeks *Adv. Phys.* **21** 693 (1977)
- [23] P P Bajpai, P N Ram and Y C Jain *J. Phys.* **C20** 5577 (1987)
- [24] K K Kobayashi *J. Phys. Soc. Jpn* **24** 497 (1968)
- [25] K R Chowdhury, D K Nath, S Banerjee and B K Chaudhuri *Phys. Rev* **B26** 6276 (1982)