Kod Projek :	FRGS/FASA2 : 203/PFIZIK/671163

BORANG FRGS – P3(R)

FINAL REPORT
FUNDAMENTAL RESEARCH GRANT SCHEME (FRGS)
Laporan Akhir Skim Geran Penyelidikan Asas (FRGS) IPT
Pindaan 1/2009

A **RESEARCH TITLE** : Theoretical and Experimental Studies of Phase Transitions (Fun-Anwar-Suchada Transition, FAST) in Hydrogen-Bonded Phenol-Amine Adducts
Tajuk Penyelidikan

PROJECT LEADER : Prof. Lee Beck Sim
Ketua Projek

PROJECT MEMBERS : 1. Prof. Fun Hoong Koon
(including GRA) 2. Prof. Madya Abdul Razak Ibrahim
Ahli Projek 3. En. Mohd. Mustaqim Rosli

PROJECT ACHIEVEMENT *(Prestasi Projek)*

B

ACHIEVEMENT PERCENTAGE

Project progress according to milestones achieved up to this period	**0 - 50%**	**51 - 75%**	**76 - 100%**
Percentage			X

RESEARCH FINDINGS

Number of articles/ manuscripts/ books	**Indexed Journal**	***Non-Indexed Journal***
	1	2
Paper presentations	**International**	***National***
	2(PACCON 2008)- Bangkok	
Others (Please specify)		

HUMAN CAPITAL DEVELOPMENT

Human Capital	**Number**		Others (Please specify):
	On-going	**Graduated**	
PhD Student			
Masters Student		1	
Undergraduate Students			
Temporary Research Officer	1		
Temporary Research Assistant			
Total	2		

EXPENDITURE *(Perbelanjaan)*

C

Budget Approved *(Peruntukan diluluskan)*	:	RM 101,200.00
Amount Spent *(Jumlah Perbelanjaan)*	:	RM 101,200.00
Balance *(Baki)*	:	RM 0.00
Percentage of Amount Spent *(Peratusan Belanja)*	:	100%

ADDITIONAL RESEARCH ACTIVITIES THAT CONTRIBUTE TOWARDS DEVELOPING SOFT AND HARD SKILLS
(Aktiviti Penyelidikan Sampingan yang menyumbang kepada pembangunan kemahiran insaniah)

D

International

Activity	Date (Month, Year)	Organizer
(e.g : Course/ Seminar/ Symposium/ Conference/ Workshop/ Site Visit)		

National

Activity	Date (Month, Year)	Organizer
(e.g : Course/ Seminar/ Symposium/ Conference/ Workshop/ Site Visit)		

PROBLEMS / CONSTRAINTS IF ANY *(Masalah/ Kekangan sekiranya ada)*

E **Experimental Problems/Constraints:** The research group has waited a long time for interest/experimental effort and results from Taiwan and Australia to complement the experimental effort and results done at USM. So far we have no received any results from the international groups needed to confirm results at USM and stimulate further progress. See **Appendix** for more details.

Theoretical Problems/Constraints: Further theoretical work on the microscopic modelling of the phase transition properties needed the input of further measurements from experimental groups outside Malaysia as mentioned above. This has delayed the theoretical progress here as new theoretical calculations can only be done to explain new experimental properties. However, further work on the phenomenological Landau theories is progressing well for the new experimental results at USM.
See **Appendix** for more details.

RECOMMENDATION *(Cadangan Penambahbaikan)*

F Taking into account the problems/constraints for experiment/theory outlined in E and the longer time frame for fundamental scientific research to develop, we recommend that the existing X-ray group and theoretical support in USM apply for further funding in future to develop the understanding of Hydrogen bonded phase transitions. This can be seen as a fundamental research effort initiated at School of Physics, USM.

RESEARCH ABSTRACT – Not More Than 200 Words(*Abstrak Penyelidikan – Tidak Melebihi 200 patah perkataan*)

G New experimental measurements on (a) a crystal code-named “spgfun44” (b) NH_4NO_3 have been made and the phase transitions found are being studied in more detail. The phenomenological theoretical description is in the process of being worked out. An alternative mean field statistical mechanical calculation has been carried out for the microscopic theory of the second order case. This confirms the theoretical results reported earlier. Further microscopic theoretical calculations depend on further experimental measurements of the phase transition properties by researchers in othercountries like Taiwan and Australia. We are still waiting for the results. A detailed understanding of the theoretical problems in the microscopic modelling has been obtained. This is important to guide further calculations in future.

Date : 14/9/09
Tarikh

Project Leader’s Signature: BS Lee
Tandatangan Ketua Projek

COMMENTS, IF ANY/ ENDORSEMENT BY RESEARCH MANAGEMENT CENTER (RMC)
(Komen, sekiranya ada/ Pengesahan oleh Pusat Pengurusan Penyelidikan)

H

....

....

....

Name: *Nama:*

Signature: *Tandatangan:*

Date: *Tarikh:*

APPENDIX

THEORETICAL STUDIES

In addition to the theoretical results which have been published, the problems have been analysed in detail and a good understanding of the theoretical issues has been achieved at present. This is important for giving a direction to ongoing and future work and will be useful for giving continuity to the theoretical research efforts, when new members have to take over the research in future.

Status of further theoretical work on microscopic modelling

Further work on microscopic theory calculations need new results of experiments on the phenomenology of the phase transitions. So far we are waiting for interest from other countries to perform the experiments. These experiments cannot be done at USM.
A group in Sydney, Australia (Bragg Institute) have started analysing the crystals with neutron diffraction. We are waiting for the final results.

We summarize the theoretical issues:

(1) **Complexity of Organic Crystals**

The structures of the phenol-amine adduct crystals are extremely complex with respect to the configurations of the hydrogen bonds. This has created very difficult problems for microscopic modelling.

(2) **Landau Phenomenological Theory**

The Landau phenomenological theories for the second order and first order cases are useful since they require no knowledge or assumptions about the microscopic interaction mechanisms [1, 2]. It is a good strategy to just use Landau theory when systems are very complex.

(3) **Microscopic Theories**

(a) The case where there is mirror symmetry breaking at the structural phase transition has been modelled to reflect only the mirror symmetry breaking caused by the hydrogen bonds [3,4] . More work needs to be done in future to analyse difficulties caused by the lack of inversion symmetry and the corresponding difficulties for the hydrogen bond – lattice interactions.

(b) The case where there is breaking of inversion symmetry and first order transition has been analysed. Due to the greater complexity of the configurations of the hyrogen bonds with no well defined characteristics, it has not been possible at present to create an acceptable microscopic model.

(c) The following experimental data *are required in future* to confirm the correctness of the model assuming H-bonds interacting with the lattice vibrations.

(i) Specific heat measurements. Estimates of the transition entropy would be able to decide whether the transition is " order-disorder" (transition entropy of the order of k ln 2) or "displacive" (transition entropy very much smaller than k ln 2).

(ii) Measurement of soft phonon modes and elastic constants. This would give useful information. When data on soft phonon modes become available, the theoretical analysis requires an extension of the model to include quantum mechanical spins.

The theoretical background for this has been given in an Internal Report [B.S.Lee , *The Pseudo-spin Formalism,* Internal Report, School of Physics, USM, 2005]

(iii) Hydrogen bond density as a function of temperature. The x-ray group have some data which shows that the hydrogen bond density has doubled below the transition temperature. This is encouraging but we need to see more data as a function of temperature. The analogy with the phase transition in a magnet is good according to the model. With magnets we have magnetization vs. temperature data. Here we need hydrogen bond density vs. temperature data.

(4) Computer Simulation Studies

Dr. Yoon Tiem Leong has started to undertake this study during his sabbatical leave in 2009. This will provide additional understanding of the H-bond system.

EXPERIMENTAL STUDIES

New experimental results:

Preliminary investigation on a sample codenamed spgfun44 and NH4NO3 has shown that it exhibits 1st order FAST with a tripling of one of the cell axis (and hence the unit cell volume).

The parameters for the high-temperature and low-temperature polymorphs are as follows:-

spgfun44

T = Room Temperature ≈ 297K in P21/c
a = 7.3660(0.0004) b = 5.1539(0.0003) c = 10.1383(0.0005)
Beta = 112.333(0.004)

T = 100K in P21/c
a = 7.3791(0.0003), b = 14.8734(0.0007), c = 10.0347(0.0005)
Beta = 111.525(0.002)

The transition temperature is from 145K to 165K.

NH4NO3

T = Room Temperature ≈ 297K in P212121
a = 8.5598(0.0006), b = 11.9546(0.0009), c = 18.3664(0.0013)

T = 100K in P212121
a = 11.7887(0.0006), b = 18.1710(0.0010), c = 25.4212(0.0015)

The transition temperature is from 101K to 103K

Further investigations are being done to narrow down the range of the transition temperature and to obtain more detailed information about the hydrogen bondings in these two polymorphs.

Work on theoretical explanation with Landau phenomenological theory is in progress.

Publications

---

1. Mohd. Mustaqim Rosli, B.S.Lee and H.K.Fun, *Mean Field Statistical Mechanics of Model Hamiltonian for Hydrogen-Bonded Phase Transitions* , Physica Status Solidi (b) **246**, No. 2, 376-382 (2009).

2. H.K.Fun (Invited Speaker), B.S.Lee and S. Chantrapromma, *Hydrogen Bonding Phase Transitions in Some Organic Crystals*, to be published in Proceedings of Pure and Applied Chemistry International Conference 2008 (PACCON 2008), 30 Jan – 1 Feb. 2008, Bangkok, Thailand.

3. B.S.Lee (contributed speaker), Mohd. Mustaqim Rosli and H.K.Fun, *Mean Field Approximations of Model Hamiltonian for Hydrogen-Bonded Phase Transitions*, to be published in Proceedings of Pure and Applied Chemistry International Conference 2008 (PACCON 2008), 30 Jan – 1 Feb. 2008, Bangkok, Thailand. (This is a very condensed version of Publication 1).

Hydrogen Bonding Phase Transitions in Some Organic Crystals

Hoong-Kun Fun[1,*] Beck-Sim Lee[1] and Suchada Chantrapromma[2]

[1]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia.
[2]Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai,
Songkhla 90112, Thailand.
**E-mail: hkfun@usm.my*

Introduction and Experimental

Our study of solid state hydrogen bonding in phenol-amine adducts and benzoic acid-amine adducts [1] has led us to discover a new type of phase transition (Fun-Anwar-Suchada Transition or abbreviated as FAST) which we attribute to originate from hydrogen bonding [1-3]. Phenols and benzoic acid (organic acids) interact with amine bases to produce many complexes rich in intramolecular and intermolecular O-H…O, O-H…N and N-H…O types of hydrogen bonds which are among the most robust and versatile synthons in crystal engineering. Some crystals of the phenol-amine adducts and benzoic acid-amine adducts undergo a distortive reversible temperature-dependent phase transition. In those crystals the structural phase transition is sometimes from orthorhombic-to-monoclinic [1, 3] ; from monoclinic-to-triclinic [1, 2]; and from triclinic to triclinic [4, 5]. We have identified and clarified the primary order parameter of these structural phase transitions and a phenomenological Landau theory of ferroelastic phase transitions was developed which was shown to be consistent with the experimental data on the temperature dependence of the unit cell parameters [1, 4, 6].

However, the analyses of experimental data strongly supported the earlier suggestion [1, 2] of the role of the formation and breaking of hydrogen bonds in these phase transitions. As is well known, the phenomenological theory, being a macroscopic theory, cannot describe the microscopic interactions causing the phase transition, although it certainly does play an important role in identifying the primary order parameter and giving insight into the overall qualitative thermodynamic behaviour of the transition.

A prototype microscopic model [7], was able to explain the main features of the phase transition, in agreement with the Landau theory of ferroelastic phase transitions. The essential physical mechanism proposed in the microscopic theory is that the interactions of the hydrogen bonds with phonons induce indirect long range interactions between the hydrogen bonds. The cooperative interactions between the hydrogen bonds drive the structural phase transition. A brief review of FAST has been published [5].

All the experimental data were collected with single-crystal x-ray diffractometer equipped with a low-temperature attachment. Full details of the experimental procedure can be found in the references [1-4, 6].

Landau Theory

The Landau phenomenological theories are usually useful for identifying the primary order parameter and characterizing the overall qualitative thermodynamic behaviour close to the transition temperature.

The Landau theories we have developed to explain the structural phase transitions assume that the free energy can be expanded in powers of the dimensionless strain components or tensors of a continuous homogeneous medium. These strain components are denoted by $e_{ij} = e_\alpha$, with $i, j = 1 \equiv x,\ 2 \equiv y,\ 3 \equiv z$. The abbreviated subscript α takes values $\alpha = 1, 2, 3, \ldots\ldots 6$ with the abbreviations $1 \equiv xx,\ 2 \equiv yy,\ 3 \equiv zz,\ 4 \equiv yz,\ 5 \equiv zx,\ 6 \equiv xy$.

For the case where the structural phase transition is from orthorhombic-to-monoclinic, and is of second order, the primary order parameter was assumed to be $e_5 \equiv e_{zx} = (\beta - \pi / 2)$, which is proportional to the small tilt in β angle. The case monoclinic-to-triclinic which is also of second order has a primary order parameter $e_4 \equiv e_{yz} = (\alpha - \pi / 2)$. The tilts in the angles β and γ are small. Details can be found in [6]. The continuous second order transitions described by the Landau phenomenological theory were found to agree with the experimental data on the temperature dependence of the unit cell parameters. It was realized that further measurements of the specific heat and elastic constants would be necessary to provide further insight into the nature of the transition.

The structural phase transition from triclinic-to-triclinic was found to involve a discontinuous change in the *c*-axis parameter and is a first order transition. There is a doubling of the *c*-axis of the unit cell below the transition temperature. The Landau theory assumes that the primary order parameter is the strain component along the *c*-axis, which is $e_3 = e_{zz}$. Since it is the strain component along the *c*-axis which must be used in the Landau theory, we have estimated the order parameter e_3 as

$$e_3 = [\ \tfrac{1}{2} \text{ value of } c \text{ below } T_c \ - \text{ value of } c \text{ above } T_c\ ] \,/\, [\ \text{value of } c \text{ above } T_c\ ]$$

The simplest form of the Landau free energy f in powers of the order parameter [4] is assumed to be

$$f - f_0(T) = \frac{1}{2}a(T)e_3^2 + \frac{1}{4}b'e_3^4 + \frac{1}{6}de_3^6 + \lambda\delta e_3^2 + \frac{1}{2}c\delta^2 + \ldots\ldots.$$

The term $f_0(T)$ is the non-ferroelastic part of the free energy. The parameters b', d, c and coupling parameter λ are assumed to be weakly temperature dependent over the range of temperatures considered and are therefore taken as constants. In considering the interaction of the primary order parameter with other strain components, we have made a simplification and considered only the last two terms in the free energy where δ represents the dilation or fractional volume change of the crystal. With this free energy we have been able to explain the main features of the first order transition. See [4] for details.

Since the phenomenological Landau theory cannot provide insight into the microscopic mechanisms causing the phase transitions, such as the suggested formation and breaking of hydrogen bonds [1, 2], attempts must be made to explain the transitions with a microscopic model. We summarize the main features of a prototype model we proposed to explain the phase transition for the second order case [7].

Qualitatively, the main features of the microscopic model are:

(a) The formation and breaking of hydrogen bonds is modeled as a two-level system using pseudo spin variables. The fluctuations in the overlap of the hydrogenic orbitals caused by lattice vibrations, taken to first order in the lattice displacements leads to interaction terms between the hydrogen bonds and lattice vibrations. In the language of a pseudo spin representation, these interactions between hydrogen bonds and lattice vibrations are described by spin-phonon interaction terms in the Hamiltonian.

(b) A mean field calculation of the thermodynamic behaviour using a variational method was able to explain the main features of the phase transition, in agreement with the Landau theory of ferroelastic phase transitions. An alternative method of calculating the thermodynamic properties of the model confirms the results of the earlier calculation [8]. The essential physical mechanism proposed in the microscopic theory is that the interactions of the hydrogen bonds with phonons induce indirect long range interactions between the hydrogen bonds. The cooperative interactions between the hydrogen bonds drive the structural phase transition.

The formation and breaking of hydrogen bonds in breaking the mirror symmetry is illustrated in Fig.1.

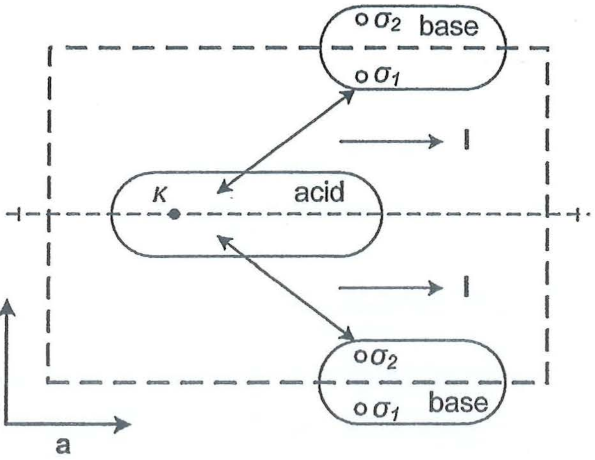

Fig.1 – The prototype phase of the crystal. The rectangular dash box represent a unit cell, and the dashed line in the middle denotes the mirror plane. With mirror symmetry, acceptor κ interacts via hydrogen atoms from both donor σ_1 and σ_2 to form or break hydrogen bonds (How et al., 2005).

A hydrogen bond is formed by the sharing of a hydrogen atom between a donor σ and an acceptor κ. The energies of the bonding states E_{bonding} and antibonding states $E_{\text{antibonding}}$ are given by

$$E_{\text{bonding}} = -E_0 - 2\mu\Delta_{\kappa\sigma}$$

$$E_{\text{antibonding}} = E_0 + 2\mu\Delta_{\kappa\sigma}$$

Note that $2E_0$ is the difference in energy between the bonding and antibonding states in the equilibrium configuration and $\Delta_{\kappa\sigma}$ is the change in energy due to the amount of overlapping of the hydrogenic orbitals caused by lattice vibrations. The coupling parameter between the hydrogen bonds and the lattice vibrations is μ. With these assumptions, the model Hamiltonian [7] can be written as

$$H = \sum_{\mathbf{k}j} \hbar\omega_{\mathbf{k}j}(a^{\dagger}_{\mathbf{k}j}a_{\mathbf{k}j}) + \sum_{\mathbf{r}}(E_0 s_{\mathbf{r}} + hw_{\mathbf{r}})$$

$$+\mu\frac{2}{\sqrt{N}}\sum_{\mathbf{r}}\sum_{\mathbf{k}j}(a_{\mathbf{k}j} + a^{\dagger}_{-\mathbf{k}j})e^{i\mathbf{k}\cdot\mathbf{r}}\sqrt{\frac{\hbar}{2\omega_{\mathbf{k}j}}}(A_{\mathbf{k}j}s_{\mathbf{r}} + B_{\mathbf{k}j}w_{\mathbf{r}})$$

The first term on RHS is harmonic phonon Hamiltonian and $a^{\dagger}_{\mathbf{k}j}$, $a_{\mathbf{k}j}$ are respectively the creation and annihilation operator of a phonon of wavevector **k** and branch j.
$s = \pm 1$ is a pseudo-spin variable to describe bonding and antibonding configurations.

(s = +1 refers to antibonding and s = -1 refers to bonding).
h is a fictitious "magnetic" field and set to zero for all physical situations. w is product of pseudo-spin s and t ($w = st$). ($t = +1$ is a pseudo-spin to label acceptor κ interacts with donor σ_1 and t = -1 labels acceptor κ interacts with donor σ_2 (see Figure x)]. The subscript **r** in $s_{\mathbf{r}}$ and $w_{\mathbf{r}}$ denotes the unit cell **r**.
N is the total number of unit cells in the crystal.

$$A_{kj} = \left(2\frac{\mathrm{e}(\kappa \mid \mathrm{k}j)}{\sqrt{m_\kappa}} - \frac{\mathrm{e}(\sigma_1 \mid \mathrm{k}j)}{\sqrt{m_\sigma}} - \frac{\mathrm{e}(\sigma_2 \mid \mathrm{k}j)}{\sqrt{m_\sigma}} \right) \cdot \mathbf{l}$$

$$B_{kj} = \left(\frac{\mathrm{e}(\sigma_2 \mid \mathrm{k}j)}{\sqrt{m_\sigma}} - \frac{\mathrm{e}(\sigma_1 \mid \mathrm{k}j)}{\sqrt{m_\sigma}} \right) \cdot \mathbf{l}$$

$\mathrm{e}(X \mid Y)$ is a phonon polarization vector. m_κ and m_σ are the mass of acceptor and donor respectively (see [9] for more details). The vector **l** is a unit vector signifying the directionality of the interaction (see How et al., [7] for more details).

Conclusion

We expect that this analysis of a prototype model of FAST caused by hydrogen bonds should have wide implications in a larger class of organic materials in molecular biology and chemistry where hydrogen bonds are plentiful and important. The type of transitions caused by indirect cooperative interactions revealed in these organic crystals adds another example of phonon-mediated transitions such as Jahn-Teller cooperative transitions and superconductivity. To our knowledge, these are the only few examples of such type of transitions so far encountered.

References

1. S. Chantrapromma. Structural Studies of Solid State Hydrogen Bonding in Adducts of Some Amine Derivatives. Ph.D. thesis, Universiti Sains Malaysia, 2004.
2. A. Usman, S. Chantrapromma & H. -K. Fun. The 143 and 300 K polymorphs of Hexamethylenetetraminium 2,4-dinitrophenolate monohydrate. *Acta Cryst.* **C57**. 2001, 1443-1446.
3. S. Chantrapromma, H. -K. Fun & A. Usman. Orthorhombic-to-monoclinic temperature-dependent phase transition of hexamethylenetetraminium-3,5-dinitrobenzoate-3,5-dinitrobenzoic acid monohydrate crystal. *J. Mol. Structure*. 2006, **789**, 30-36.
4. H. –K. Fun, Mohd Mustaqim Rosli, Beck-Sim Lee, Lye-Hock Ong, Suchada Chantrapromma.
   First order temperature-dependent phase transition of hexamethylenetetraminium 3,5 dinitrobenzoate hemihydrate crystal: Landau phenomenological theory approach. *J. Mol. Structure*. 2007, **837**, 132-141.
5. H. –K. Fun, B. –S. Lee and S. Chantrapromma. Hydrogen Bonding Phase Transistions in

Some Organic Crystals. *Ferroelectrics* 2007, **349**, 45-48.

6. H. -K. Fun, A. Usman, S. Chantrapromma, J. Osman, L.-H. Ong, D. R. Tilley & Y. Ishibashi. Phase transitions in hydrogen-bonded phenol-amine adducts: analysis by ferroelastic theory. *Solid State Comm.* 2003, **127**, 677-682.
7. P. -T. How, B. -S. Lee, H. -K. Fun, I. A. Razak, S. Chantrapromma. Microscopic theory of phase transitions in hydrogen-bonded phenol-amine adducts. *Phys. Rev. B.* 2005. **71**, 174109.
8. Mohd Mustaqim Rosli. Study of Hydrogen Bondings in Phenol-Amines Adducts, M.Sc. thesis, Universiti Sains Malaysia, 2008.
9. A. A. Maradudin, E. W. Montroll and G. H. Weiss, Theory of Lattice Dynamics in the Harmonic Approximation, 1971, Academic, New York.

Hydrogen Bonding Phase Transitions in Some Organic Crystals

Hoong-Kun Fun[1,*] Beck-Sim Lee[1] and Suchada Chantrapromma[2]

[1]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia.*
[2]*Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai,*
Songkhla 90112, Thailand.
**E-mail: hkfun@usm.my*

Introduction and Experimental

Our study of solid state hydrogen bonding in phenol-amine adducts and benzoic acid-amine adducts [1] has led us to discover a new type of phase transition (Fun-Anwar-Suchada Transition or abbreviated as FAST) which we attribute to originate from hydrogen bonding [1-3]. Phenols and benzoic acid (organic acids) interact with amine bases to produce many complexes rich in intramolecular and intermolecular O-H…O, O-H…N and N-H…O types of hydrogen bonds which are among the most robust and versatile synthons in crystal engineering. Some crystals of the phenol-amine adducts and benzoic acid-amine adducts undergo a distortive reversible temperature-dependent phase transition. In those crystals the structural phase transition is sometimes from orthorhombic-to-monoclinic [1, 3] ; from monoclinic-to-triclinic [1, 2]; and from triclinic to triclinic [4, 5]. We have identified and clarified the primary order parameter of these structural phase transitions and a phenomenological Landau theory of ferroelastic phase transitions was developed which was shown to be consistent with the experimental data on the temperature dependence of the unit cell parameters [1, 4, 6].

However, the analyses of experimental data strongly supported the earlier suggestion [1, 2] of the role of the formation and breaking of hydrogen bonds in these phase transitions. As is well known, the phenomenological theory, being a macroscopic theory, cannot describe the microscopic interactions causing the phase transition, although it certainly does play an important role in identifying the primary order parameter and giving insight into the overall qualitative thermodynamic behaviour of the transition.

A prototype microscopic model [7], was able to explain the main features of the phase transition, in agreement with the Landau theory of ferroelastic phase transitions. The essential physical mechanism proposed in the microscopic theory is that the interactions of the hydrogen bonds with phonons induce indirect long range interactions between the hydrogen bonds. The cooperative interactions between the hydrogen bonds drive the structural phase transition. A brief review of FAST has been published [5].

All the experimental data were collected with single-crystal x-ray diffractometer equipped with a low-temperature attachment. Full details of the experimental procedure can be found in the references [1-4, 6].

Landau Theory

The Landau phenomenological theories are usually useful for identifying the primary order parameter and characterizing the overall qualitative thermodynamic behaviour close to the transition temperature.

The Landau theories we have developed to explain the structural phase transitions assume that the free energy can be expanded in powers of the dimensionless strain components or tensors of a continuous homogeneous medium. These strain components are denoted by $e_{ij} = e_\alpha$, with $i, j = 1 \equiv x,\ 2 \equiv y,\ 3 \equiv z$. The abbreviated subscript α takes values $\alpha = 1, 2, 3, \ldots\ldots 6$ with the abbreviations $1 \equiv xx,\ 2 \equiv yy,\ 3 \equiv zz,\ 4 \equiv yz,\ 5 \equiv zx,\ 6 \equiv xy$.

For the case where the structural phase transition is from orthorhombic-to-monoclinic, and is of second order, the primary order parameter was assumed to be $e_5 \equiv e_{zx} = (\beta - \pi/2)$, which is proportional to the small tilt in β angle. The case monoclinic-to-triclinic which is also of second order has a primary order parameter $e_4 \equiv e_{yz} = (\alpha - \pi/2)$. The tilts in the angles β and γ are small. Details can be found in [6]. The continuous second order transitions described by the Landau phenomenological theory were found to agree with the experimental data on the temperature dependence of the unit cell parameters. It was realized that further measurements of the specific heat and elastic constants would be necessary to provide further insight into the nature of the transition.

The structural phase transition from triclinic-to-triclinic was found to involve a discontinuous change in the *c*-axis parameter and is a first order transition. There is a doubling of the *c*-axis of the unit cell below the transition temperature. The Landau theory assumes that the primary order parameter is the strain component along the *c*-axis, which is $e_3 = e_{zz}$. Since it is the strain component along the *c*-axis which must be used in the Landau theory, we have estimated the order parameter e_3 as

$$e_3 = [\ \tfrac{1}{2} \text{ value of } c \text{ below } T_c \ - \text{ value of } c \text{ above } T_c\ ] \,/\, [\ \text{value of } c \text{ above } T_c\ ]$$

The simplest form of the Landau free energy f in powers of the order parameter [4] is assumed to be

$$f - f_0(T) = \frac{1}{2}a(T)e_3^2 + \frac{1}{4}b'e_3^4 + \frac{1}{6}de_3^6 + \lambda\delta e_3^2 + \frac{1}{2}c\delta^2 + \ldots\ldots$$

The term $f_0(T)$ is the non-ferroelastic part of the free energy. The parameters b', d, c and coupling parameter λ are assumed to be weakly temperature dependent over the range of temperatures considered and are therefore taken as constants. In considering the interaction of the primary order parameter with other strain components, we have made a simplification and considered only the last two terms in the free energy where δ represents the dilation or fractional volume change of the crystal. With this free energy we have been able to explain the main features of the first order transition. See [4] for details.

Microscopic Theory

Since the phenomenological Landau theory cannot provide insight into the microscopic mechanisms causing the phase transitions, such as the suggested formation and breaking of hydrogen bonds [1, 2], attempts must be made to explain the transitions with a microscopic model. We summarize the main features of a prototype model we proposed to explain the phase transition for the second order case [7].

Qualitatively, the main features of the microscopic model are:

(a) The formation and breaking of hydrogen bonds is modeled as a two-level system using pseudo spin variables. The fluctuations in the overlap of the hydrogenic orbitals caused by lattice vibrations, taken to first order in the lattice displacements leads to interaction terms between the hydrogen bonds and lattice vibrations. In the language of a pseudo spin representation, these interactions between hydrogen bonds and lattice vibrations are described by spin-phonon interaction terms in the Hamiltonian.

(b) A mean field calculation of the thermodynamic behaviour using a variational method was able to explain the main features of the phase transition, in agreement with the Landau theory of ferroelastic phase transitions. An alternative method of calculating the thermodynamic properties of the model confirms the results of the earlier calculation [8]. The essential physical mechanism proposed in the microscopic theory is that the interactions of the hydrogen bonds with phonons induce indirect long range interactions between the hydrogen bonds. The cooperative interactions between the hydrogen bonds drive the structural phase transition.

The formation and breaking of hydrogen bonds in breaking the mirror symmetry is illustrated in Fig.1.

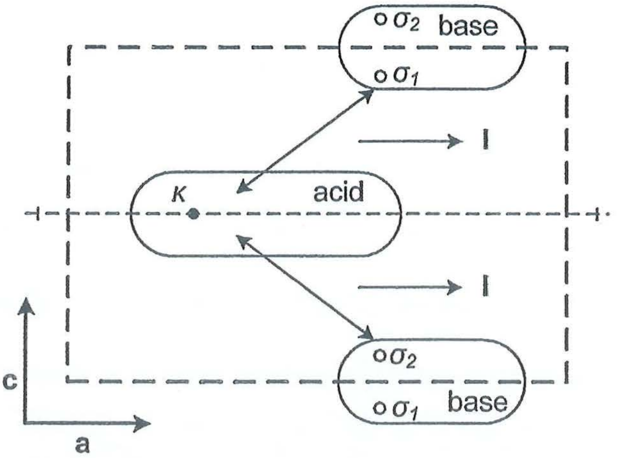

Fig.1 – The prototype phase of the crystal. The rectangular dash box represent a unit cell, and the dashed line in the middle denotes the mirror plane. With mirror symmetry, acceptor κ interacts via hydrogen atoms from both donor σ_1 and σ_2 to form or break hydrogen bonds (How et al., 2005).

A hydrogen bond is formed by the sharing of a hydrogen atom between a donor σ and an acceptor κ. The energies of the bonding states E_{bonding} and antibonding states $E_{\text{antibonding}}$ are given by

$$E_{\text{bonding}} = -E_0 - 2\mu\Delta_{\kappa\sigma}$$

$$E_{\text{antibonding}} = E_0 + 2\mu\Delta_{\kappa\sigma}$$

Note that $2E_0$ is the difference in energy between the bonding and antibonding states in the equilibrium configuration and $\Delta_{\kappa\sigma}$ is the change in energy due to the amount of overlapping of the hydrogenic orbitals caused by lattice vibrations. The coupling parameter between the hydrogen bonds and the lattice vibrations is μ. With these assumptions, the model Hamiltonian [7] can be written as

$$H = \sum_{\mathbf{k}j} \hbar\omega_{\mathbf{k}j}(a^{\dagger}_{\mathbf{k}j}a_{\mathbf{k}j}) + \sum_{\mathbf{r}}(E_0 s_{\mathbf{r}} + hw_{\mathbf{r}})$$

$$+\mu\frac{2}{\sqrt{N}}\sum_{\mathbf{r}}\sum_{\mathbf{k}j}(a_{\mathbf{k}j} + a^{\dagger}_{-\mathbf{k}j})e^{i\mathbf{k}\cdot\mathbf{r}}\sqrt{\frac{\hbar}{2\omega_{\mathbf{k}j}}}(A_{\mathbf{k}j}s_{\mathbf{r}} + B_{\mathbf{k}j}w_{\mathbf{r}})$$

The first term on RHS is harmonic phonon Hamiltonian and $a^{\dagger}_{\mathbf{k}j}$, $a_{\mathbf{k}j}$ are respectively the creation and annihilation operator of a phonon of wavevector **k** and branch j.

$s = \pm 1$ is a pseudo-spin variable to describe bonding and antibonding configurations.

(s = +1 refers to antibonding and s = -1 refers to bonding).
h is a fictitious "magnetic" field and set to zero for all physical situations. w is product of pseudo-spin s and t ($w = st$). ($t = +1$ is a pseudo-spin to label acceptor κ interacts with donor σ_1 and t = -1 labels acceptor κ interacts with donor σ_2 (see Figure x)]. The subscript $\mathbf{r}$ in $s_\mathbf{r}$ and $w_\mathbf{r}$ denotes the unit cell $\mathbf{r}$.
N is the total number of unit cells in the crystal.

$$A_{\mathbf{k}j} = \left(2\frac{\mathbf{e}(\kappa\,|\,\mathbf{k}j)}{\sqrt{m_\kappa}} - \frac{\mathbf{e}(\sigma_1\,|\,\mathbf{k}j)}{\sqrt{m_\sigma}} - \frac{\mathbf{e}(\sigma_2\,|\,\mathbf{k}j)}{\sqrt{m_\sigma}} \right)\cdot\mathbf{l}$$

$$B_{\mathbf{k}j} = \left(\frac{\mathbf{e}(\sigma_2\,|\,\mathbf{k}j)}{\sqrt{m_\sigma}} - \frac{\mathbf{e}(\sigma_1\,|\,\mathbf{k}j)}{\sqrt{m_\sigma}} \right)\cdot\mathbf{l}$$

$\mathbf{e}(X\,|\,Y)$ is a phonon polarization vector. m_κ and m_σ are the mass of acceptor and donor respectively (see [9] for more details). The vector $\mathbf{l}$ is a unit vector signifying the directionality of the interaction (see How et al., [7] for more details).

Conclusion

We expect that this analysis of a prototype model of FAST caused by hydrogen bonds should have wide implications in a larger class of organic materials in molecular biology and chemistry where hydrogen bonds are plentiful and important. The type of transitions caused by indirect cooperative interactions revealed in these organic crystals adds another example of phonon-mediated transitions such as Jahn-Teller cooperative transitions and superconductivity. To our knowledge, these are the only few examples of such type of transitions so far encountered.

References

1. S. Chantrapromma. Structural Studies of Solid State Hydrogen Bonding in Adducts of Some Amine Derivatives. Ph.D. thesis, Universiti Sains Malaysia, 2004.
2. A. Usman, S. Chantrapromma & H. -K. Fun. The 143 and 300 K polymorphs of Hexamethylenetetraminium 2,4-dinitrophenolate monohydrate.
   Acta Cryst. C57. 2001, 1443-1446.
3. S. Chantrapromma, H. -K. Fun & A. Usman. Orthorhombic-to-monoclinic temperature-dependent phase transition of hexamethylenetetraminium-3,5-dinitrobenzoate-3,5-dinitrobenzoic acid monohydrate crystal. *J. Mol. Structure*. 2006, **789**, 30-36.
4. H. –K. Fun, Mohd Mustaqim Rosli, Beck-Sim Lee, Lye-Hock Ong, Suchada Chantrapromma.
   First order temperature-dependent phase transition of hexamethylenetetraminium 3,5 dinitrobenzoate hemihydrate crystal: Landau phenomenological theory approach.
   J. Mol. Structure. 2007, **837**, 132-141.
5. H. –K. Fun, B. –S. Lee and S. Chantrapromma. Hydrogen Bonding Phase Transistions in

Some Organic Crystals. *Ferroelectrics* 2007, **349**, 45-48.

6. H. -K. Fun, A. Usman, S. Chantrapromma, J. Osman, L.-H. Ong, D. R. Tilley & Y. Ishibashi. Phase transitions in hydrogen-bonded phenol-amine adducts: analysis by ferroelastic theory. *Solid State Comm.* 2003, **127**, 677-682.
7. P. -T. How, B. -S. Lee, H. -K. Fun, I. A. Razak, S. Chantrapromma. Microscopic theory of phase transitions in hydrogen-bonded phenol-amine adducts. *Phys. Rev. B*. 2005. **71**, 174109.
8. Mohd Mustaqim Rosli. Study of Hydrogen Bondings in Phenol-Amines Adducts, M.Sc. thesis, Universiti Sains Malaysia, 2008.
9. A. A. Maradudin, E. W. Montroll and G. H. Weiss, Theory of Lattice Dynamics in the Harmonic Approximation, 1971, Academic, New York.

Mean Field Approximations of Model Hamiltonian for Hydrogen-Bonded Phase Transitions

Beck Sim Lee, Mohd Mustaqim Rosli and Hoong Kun Fun
School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
E-mail: leebs@streamyx.com

ABSTRACT

A new prototype microscopic model involving the formation and breaking of hydrogen bonds in some organic crystals of hydrogen bonded phenol-amine adducts has been proposed recently to explain the structural phase transitions observed. A variational calculation of the thermodynamic properties was able to explain the main features of the phase transitions. We report an alternative statistical mechanical calculation which confirms the results of the earlier calculation. In this calculation self –energy terms in the free energy which were not present in the earlier calculation need to be subtracted off.

Keywords
Hydrogen bonds, organic crystals, phenol-amine adducts, structural phase transitions, microscopic model, variational calculation.

1. INTRODUCTION

A microscopic model was recently proposed [1] to explain structural phase transitions in a class of hydrogen-bonded organic crystals called phenol-amine adducts. The organic phenol-amine adducts [2,3] are simpler in structure than the generally more complicated biological systems. Phase transitions in these organic materials could possibly be caused by similar mechanisms involving hydrogen bonds and phonons as described in the prototype model since hydrogen bonds exist in all organic materials in chemistry and molecular biology [4].

The variational method of calculation of the statistical mechanical properties used a method developed for general spin-phonon problems [6,7] and is expected to give a mean field type of approximation. However, since this calculation is the first analysis of the newly proposed model Hamiltonian, other methods of analysis would in principle be useful for further checks on the behavior of the model. In this paper we report the results of an alternative calculation. A complete decoupling of the pseudo-spin terms from the phonon terms is done to give an effective spin Hamiltonian. A variational calculation is done on the effective spin Hamiltonian. It is found that self-energy terms which did not appear in the previous calculation now appear. After subtracting off these self-energy terms, the results agree with the previous calculation. This provides confirmation of the earlier results of calculation.

2. MODEL HAMILTONIAN

Qualitatively, the main features of the microscopic model proposed are:

The formation and breaking of hydrogen bonds is modeled as a two-level system using pseudo spin variables. Fluctuations in the overlap of the hydrogenic orbitals caused by lattice vibrations, taken to first order in the lattice displacements leads to interaction terms between the hydrogen bonds and phonons of the crystal . This mechanism creates spin-phonon interaction terms in the Hamiltonian. We summarize very briefly the microscopic model [1].

The formation and breaking of hydrogen bonds is illustrated in Figure.1.

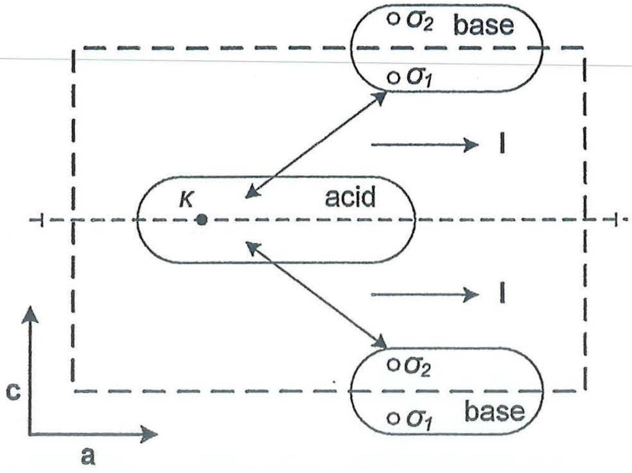

Figure 1. The prototype phase of the crystal. The rectangular dashbox represent a unit cell, and the dashed line in the middle denotes the mirror plane. Acceptor κ interacts via a hydrogen atom H in between donor σ_1 or σ_2 to form or break a hydrogen bond [1].

A hydrogen bond is formed by the sharing of a hydrogen atom between a donor σ and an acceptor κ. The energies of the bonding states E_{bonding} and antibonding states $E_{\text{antibonding}}$ are given by

$$E_{\text{bonding}} = -E_0 - 2\mu\Delta_{\kappa\sigma} \tag{1}$$

$$E_{\text{antibonding}} = E_0 + 2\mu\Delta_{\kappa\sigma} \tag{2}$$

Here $2E_0$ is the difference in energy between the bonding and antibonding states in the equilibrium configuration and $\Delta_{\kappa\sigma}$ is the change in energy due to the degree of overlapping of the hydrogenic orbitals caused by lattice vibrations. The coupling parameter between the hydrogen bonds and the lattice vibrations is μ. A single equation for H_h, the hydrogen bond energy,

$$H_h = (E_0 + 2\mu\Delta_{\kappa\sigma})s \tag{3}$$

describes the formation and breaking of hydrogen bonds by using the pseudo spin variable $s = \pm 1$, where $s = +1$ represents the antibonding state and $s = -1$ represents the bonding state.
Four states are possible in the prototype phase described in Fig. 1, and we need to introduce another pseudo spin variable $t = \pm 1$, where $t = +1$ represents the two states where κ is bonding or antibonding with σ_1. The value $t = -1$ represents the two states where κ is bonding or antibonding with σ_2.
With these assumptions, the model Hamiltonian [1, 5] can be written as

$$H = \sum_{\mathrm{k}j} \hbar\omega_{\mathrm{k}j}(a^{\dagger}_{\mathrm{k}j}a_{\mathrm{k}j}) + \sum_{\mathrm{r}}(E_0 s_{\mathrm{r}} + hw_{\mathrm{r}})$$
$$+\mu\frac{2}{\sqrt{N}}\sum_{\mathrm{r}}\sum_{\mathrm{k}j}(a_{\mathrm{k}j} + a^{\dagger}_{-\mathrm{k}j})e^{i\mathbf{k}\cdot\mathbf{r}}\sqrt{\frac{\hbar}{2\omega_{\mathrm{k}j}}}(A_{\mathrm{k}j}s_{\mathrm{r}} + B_{\mathrm{k}j}w_{\mathrm{r}}) \tag{4}$$

The first term on RHS is the harmonic phonon Hamiltonian and $a^{\dagger}_{\mathbf{k}j}$, $a_{\mathbf{k}j}$ are respectively the creation and annihilation operator of a phonon of wavevector **k** and branch j.

h is a fictitious "magnetic" field and is set to zero for all physical situations. The symbol $s_{\mathbf{r}}$ denotes the s spin in unit cell **r** and $w_{\mathbf{r}}$ denotes the w spin in unit cell **r**. Here the w pseudo spin variable is defined as $w = st$ and it is more covenient to consider s and w as independent variables rather than the original s and t . N is the total number of unit cells in the crystal.

$$A_{\mathbf{k}j} = \left(2\frac{\mathbf{e}(\kappa \mid \mathbf{k}j)}{\sqrt{m_{\kappa}}} - \frac{\mathbf{e}(\sigma_1 \mid \mathbf{k}j)}{\sqrt{m_{\sigma}}} - \frac{\mathbf{e}(\sigma_2 \mid \mathbf{k}j)}{\sqrt{m_{\sigma}}} \right) \cdot \mathbf{l}$$

$$B_{\mathbf{k}j} = \left(\frac{\mathbf{e}(\sigma_2 \mid \mathbf{k}j)}{\sqrt{m_{\sigma}}} - \frac{\mathbf{e}(\sigma_1 \mid \mathbf{k}j)}{\sqrt{m_{\sigma}}} \right) \cdot \mathbf{l}$$

$\mathbf{e}(x \mid y)$ is a phonon polarization vector. m_{κ} and m_{σ} are the mass of acceptor and donor respectively [8]. The vector **l** is a unit vector signifying the directionality of the interaction. See [1] for more details.

3. EFFECTIVE SPIN HAMILTONIAN

We apply a canonical transformation to make linear terms in the phonon operators in Eq. (4) disappear. New phonon operators $b_{\mathbf{k}j}$ and $b^{\dagger}_{\mathbf{k}j}$ are defined by

$$a_{\mathbf{k}j} \to b_{\mathbf{k}j} = a_{\mathbf{k}j} + c_{\mathbf{k}j}\,, \text{ or } a_{\mathbf{k}j} = b_{\mathbf{k}j} - c_{\mathbf{k}j} \tag{5a}$$

$$a^{\dagger}_{\mathbf{k}j} \to b^{\dagger}_{\mathbf{k}j} = a^{\dagger}_{\mathbf{k}j} + c^{\dagger}_{\mathbf{k}j}\,, \text{ or } a^{\dagger}_{\mathbf{k}j} = b^{\dagger}_{\mathbf{k}j} - c^{\dagger}_{\mathbf{k}j} \tag{5b}$$

where $c_{\mathbf{k}j}$ are c-numbers. The $b_{\mathbf{k}j}$ and $b^{\dagger}_{\mathbf{k}j}$ satisfy the same commutation relations as $a_{\mathbf{k}j}$ and $a^{\dagger}_{\mathbf{k}j}$ since the pseudo spin variables are in fact classical variables which commute with one another.

Substituting (5a) and (5b) in (4), we get the effective spin Hamiltonian in which spin parts have been separated completely from the phonon parts. We can calculate the thermodynamic properties of the system from this effective spin Hamiltonian

$$H_s = \sum_{\mathbf{r}} (E_o s_{\mathbf{r}} + h w_{\mathbf{r}}) - \frac{4\mu^2}{N} \sum_{\mathbf{k}j} \sum_{\mathbf{r}} \frac{1}{2\omega^2_{\mathbf{k}j}} [A_{\mathbf{k}j} A_{\mathbf{-k}j} + B_{\mathbf{k}j} B_{\mathbf{-k}j} + (A_{\mathbf{k}j} B_{\mathbf{-k}j} + A_{\mathbf{-k}j} B_{\mathbf{k}j}) s_{\mathbf{r}} w_{\mathbf{r}}]$$

$$- \frac{4\mu^2}{N} \sum_{\mathbf{k}j} \sum_{\mathbf{r}} \sum_{\mathbf{r}' \neq \mathbf{r}} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \frac{1}{2\omega^2_{\mathbf{k}j}} (A_{\mathbf{k}j} A_{\mathbf{-k}j} s_{\mathbf{r}} s_{\mathbf{r}'} + A_{\mathbf{k}j} B_{\mathbf{-k}j} s_{\mathbf{r}} w_{\mathbf{r}'}$$

$$+ A_{\mathbf{-k}j} B_{\mathbf{k}j} s_{\mathbf{r}'} w_{\mathbf{r}} + B_{\mathbf{k}j} B_{\mathbf{-k}j} w_{\mathbf{r}} w_{\mathbf{r}'}) \tag{6}$$

4. VARIATIONAL CALCULATION

We use the Gibbs-Bogolyubov inequality [6,7, and references therein] to calculate an upper bound to the free energy of the effective spin system. Details of the calculation are too long to be described here and can be found in reference [5].

The trial Hamiltonian H_t is chosen to be

$$H_t = \sum_{\mathbf{r}} (v_{\mathbf{r}} s_{\mathbf{r}} + \eta_{\mathbf{r}} w_{\mathbf{r}}) \tag{7}$$

where $v_{\mathbf{r}}$ and $\eta_{\mathbf{r}}$ are variational parameters.

Note that the earlier calculation [1] used a trial Hamiltonian involving both spin and phonon variables with four variational parameters and does not go through the process of obtaining an explicit effective spin Hamiltonian as is done here. After minimising the free energy upper bound with respect to the variational parameters, we obtain results which agree with the previous calculation after subtracting off self-energy terms. The self-energy terms do not appear in the earlier calculation. We have therefore confirmed the results of the earlier calculation with the alternative calculation here.

5. ACKNOWLEDGEMENTS

The authors thank the Malaysian Government and Universiti Sains Malaysia for the Fundamental Research Grant Scheme (FRGS) (Acc. No. 203/PFIZIK/671163) and the Scientific Advancement Grant Allocation (SAGA) Grant No. 304/PFIZIK/635003/A118.

6. REFERENCES

1. P. T. How, B. S. Lee, H. K. Fun, I. A. Razak and S. Chantrapromma, *Phys. Rev.* **2005,** B71, 174109 .
2. A. Usman, S. Chantrapromma and H. K. Fun, *Acta Cryst.* **2001,** C57, 1443.
3. H. K. Fun, B. S. Lee and S. Chantrapromma, *Ferroelectrics.* **2007,** 349, 45.
4. G. A. Jeffrey, *An Introduction to Hydrogen Bonding* . Oxford University Press, New York, **1997.**
5. Mohd Mustaqim Rosli. Study of Hydrogen Bondings in Phenol-Amine Adducts, *M.Sc thesis,* Universiti Sains Malaysia, Penang, Malaysia, **2008.**
6. B. S. Lee, *J. Low Temp. Phys.* **1973,** 13, 81.
7. B. S. Lee, *J. Phys. C.* **1980,** 13, 2651.
8. A. A. Maradudin, E. W. Montroll and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation.* Academic Press, New York, **1971.**

Mean Field Approximations of Model Hamiltonian for Hydrogen-Bonded Phase Transitions

Beck Sim Lee, Mohd Mustaqim Rosli and Hoong Kun Fun
School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
E-mail: leebs@streamyx.com

ABSTRACT

A new prototype microscopic model involving the formation and breaking of hydrogen bonds in some organic crystals of hydrogen bonded phenol-amine adducts has been proposed recently to explain the structural phase transitions observed. A variational calculation of the thermodynamic properties was able to explain the main features of the phase transitions. We report an alternative statistical mechanical calculation which confirms the results of the earlier calculation. In this calculation self –energy terms in the free energy which were not present in the earlier calculation need to be subtracted off.

Keywords
Hydrogen bonds, organic crystals, phenol-amine adducts, structural phase transitions, microscopic model, variational calculation.

1. INTRODUCTION

A microscopic model was recently proposed [1] to explain structural phase transitions in a class of hydrogen-bonded organic crystals called phenol-amine adducts. The organic phenol-amine adducts [2,3] are simpler in structure than the generally more complicated biological systems. Phase transitions in these organic materials could possibly be caused by similar mechanisms involving hydrogen bonds and phonons as described in the prototype model since hydrogen bonds exist in all organic materials in chemistry and molecular biology [4].

The variational method of calculation of the statistical mechanical properties used a method developed for general spin-phonon problems [6,7] and is expected to give a mean field type of approximation. However, since this calculation is the first analysis of the newly proposed model Hamiltonian, other methods of analysis would in principle be useful for further checks on the behavior of the model. In this paper we report the results of an alternative calculation. A complete decoupling of the pseudo-spin terms from the phonon terms is done to give an effective spin Hamiltonian. A variational calculation is done on the effective spin Hamiltonian. It is found that self-energy terms which did not appear in the previous calculation now appear. After subtracting off these self-energy terms, the results agree with the previous calculation. This provides confirmation of the earlier results of calculation.

2. MODEL HAMILTONIAN

Qualitatively, the main features of the microscopic model proposed are:

The formation and breaking of hydrogen bonds is modeled as a two-level system using pseudo spin variables. Fluctuations in the overlap of the hydrogenic orbitals caused by lattice vibrations, taken to first order in the lattice displacements leads to interaction terms between the hydrogen bonds and phonons of the crystal . This mechanism creates spin-phonon interaction terms in the Hamiltonian. We summarize very briefly the microscopic model [1].

The formation and breaking of hydrogen bonds is illustrated in Figure.1.

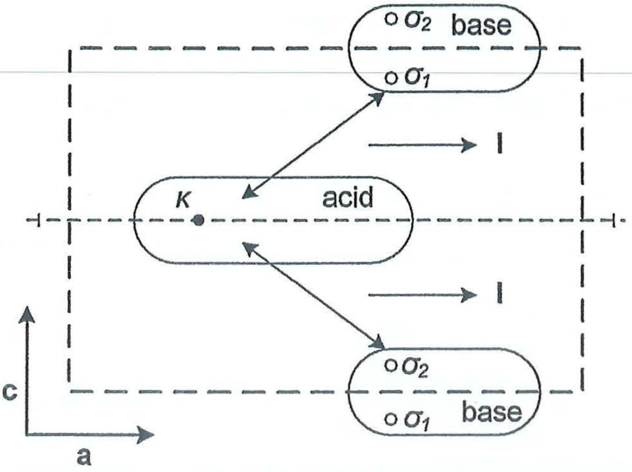

Figure 1. The prototype phase of the crystal. The rectangular dashbox represent a unit cell, and the dashed line in the middle denotes the mirror plane. Acceptor κ interacts via a hydrogen atom H in between donor σ_1 or σ_2 to form or break a hydrogen bond [1].

A hydrogen bond is formed by the sharing of a hydrogen atom between a donor σ and an acceptor κ. The energies of the bonding states E_{bonding} and antibonding states $E_{\text{antibonding}}$ are given by

$$E_{\text{bonding}} = -E_0 - 2\mu\Delta_{\kappa\sigma} \tag{1}$$

$$E_{\text{antibonding}} = E_0 + 2\mu\Delta_{\kappa\sigma} \tag{2}$$

Here $2E_0$ is the difference in energy between the bonding and antibonding states in the equilibrium configuration and $\Delta_{\kappa\sigma}$ is the change in energy due to the degree of overlapping of the hydrogenic orbitals caused by lattice vibrations. The coupling parameter between the hydrogen bonds and the lattice vibrations is μ. A single equation for H_h, the hydrogen bond energy,

$$H_h = (E_0 + 2\mu\Delta_{\kappa\sigma})s \tag{3}$$

describes the formation and breaking of hydrogen bonds by using the pseudo spin variable $s = \pm 1$, where $s = +1$ represents the antibonding state and $s = -1$ represents the bonding state.

Four states are possible in the prototype phase described in Fig. 1, and we need to introduce another pseudo spin variable $t = \pm 1$, where $t = +1$ represents the two states where κ is bonding or antibonding with σ_1. The value $t = -1$ represents the two states where κ is bonding or antibonding with σ_2.

With these assumptions, the model Hamiltonian [1, 5] can be written as

$$H = \sum_{\mathbf{k}j} \hbar\omega_{\mathbf{k}j}(a^{\dagger}_{\mathbf{k}j}a_{\mathbf{k}j}) + \sum_{\mathbf{r}} (E_0 s_{\mathbf{r}} + h w_{\mathbf{r}})$$

$$+\mu\frac{2}{\sqrt{N}}\sum_{\mathbf{r}}\sum_{\mathbf{k}j}(a_{\mathbf{k}j} + a^{\dagger}_{-\mathbf{k}j})e^{i\mathbf{k}\cdot\mathbf{r}}\sqrt{\frac{\hbar}{2\omega_{\mathbf{k}j}}}(A_{\mathbf{k}j}s_{\mathbf{r}} + B_{\mathbf{k}j}w_{\mathbf{r}}) \tag{4}$$

The first term on RHS is the harmonic phonon Hamiltonian and $a_{\mathbf{k}j}^{\dagger}$, $a_{\mathbf{k}j}$ are respectively the creation and annihilation operator of a phonon of wavevector **k** and branch *j*.
h is a fictitious "magnetic" field and is set to zero for all physical situations. The symbol $s_{\mathbf{r}}$ denotes the *s* spin in unit cell **r** and $w_{\mathbf{r}}$ denotes the *w* spin in unit cell **r**. Here the *w* pseudo spin variable is defined as *w* =*st* and it is more covenient to consider *s* and *w* as independent variables rather than the original *s* and *t* . *N* is the total number of unit cells in the crystal.

$$A_{\mathbf{k}j} = \left(2\frac{\mathbf{e}(\kappa\,|\,\mathbf{k}j)}{\sqrt{m_\kappa}} - \frac{\mathbf{e}(\sigma_1\,|\,\mathbf{k}j)}{\sqrt{m_\sigma}} - \frac{\mathbf{e}(\sigma_2\,|\,\mathbf{k}j)}{\sqrt{m_\sigma}} \right) \cdot \mathbf{l}$$

$$B_{\mathbf{k}j} = \left(\frac{\mathbf{e}(\sigma_2\,|\,\mathbf{k}j)}{\sqrt{m_\sigma}} - \frac{\mathbf{e}(\sigma_1\,|\,\mathbf{k}j)}{\sqrt{m_\sigma}} \right) \cdot \mathbf{l}$$

$\mathbf{e}(x\,|\,y)$ is a phonon polarization vector. m_κ and m_σ are the mass of acceptor and donor respectively [8]. The vector **l** is a unit vector signifying the directionality of the interaction. See [1] for more details.

3. EFFECTIVE SPIN HAMILTONIAN

We apply a canonical transformation to make linear terms in the phonon operators in Eq. (4) disappear. New phonon operators $b_{\mathbf{k}j}$ and $b_{\mathbf{k}j}^{\dagger}$ are defined by

$$a_{\mathbf{k}j} \rightarrow b_{\mathbf{k}j} = a_{\mathbf{k}j} + c_{\mathbf{k}j}\,,\ \text{or}\ a_{\mathbf{k}j} = b_{\mathbf{k}j} - c_{\mathbf{k}j} \tag{5a}$$

$$a_{\mathbf{k}j}^{\dagger} \rightarrow b_{\mathbf{k}j}^{\dagger} = a_{\mathbf{k}j}^{\dagger} + c_{\mathbf{k}j}^{\dagger}\,,\ \text{or}\ a_{\mathbf{k}j}^{\dagger} = b_{\mathbf{k}j}^{\dagger} - c_{\mathbf{k}j}^{\dagger} \tag{5b}$$

where $c_{\mathbf{k}j}$ are c-numbers. The $b_{\mathbf{k}j}$ and $b_{\mathbf{k}j}^{\dagger}$ satisfy the same commutation relations as $a_{\mathbf{k}j}$ and $a_{\mathbf{k}j}^{\dagger}$ since the pseudo spin variables are in fact classical variables which commute with one another.
Substituting (5a) and (5b) in (4), we get the effective spin Hamiltonian in which spin parts have been separated completely from the phonon parts. We can calculate the thermodynamic properties of the system from this effective spin Hamiltonian

$$H_s = \sum_{\mathbf{r}} (E_o s_{\mathbf{r}} + h w_{\mathbf{r}}) - \frac{4\mu^2}{N} \sum_{\mathbf{k}j} \sum_{\mathbf{r}} \frac{1}{2\omega_{\mathbf{k}j}^2} [A_{\mathbf{k}j} A_{\text{-}\mathbf{k}j} + B_{\mathbf{k}j} B_{\text{-}\mathbf{k}j} + (A_{\mathbf{k}j} B_{\text{-}\mathbf{k}j} + A_{\text{-}\mathbf{k}j} B_{\mathbf{k}j}) s_{\mathbf{r}} w_{\mathbf{r}}]$$

$$-\frac{4\mu^2}{N} \sum_{\mathbf{k}j} \sum_{\mathbf{r}} \sum_{\mathbf{r}'\neq\mathbf{r}} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \frac{1}{2\omega_{\mathbf{k}j}^2} (A_{\mathbf{k}j} A_{\text{-}\mathbf{k}j} s_{\mathbf{r}} s_{\mathbf{r}'} + A_{\mathbf{k}j} B_{\text{-}\mathbf{k}j} s_{\mathbf{r}} w_{\mathbf{r}'}$$

$$+ A_{\text{-}\mathbf{k}j} B_{\mathbf{k}j} s_{\mathbf{r}'} w_{\mathbf{r}} + B_{\mathbf{k}j} B_{\text{-}\mathbf{k}j} w_{\mathbf{r}} w_{\mathbf{r}'}) \tag{6}$$

4. VARIATIONAL CALCULATION

We use the Gibbs-Bogolyubov inequality [6,7, and references therein] to calculate an upper bound to the free energy of the effective spin system. Details of the calculation are too long to be described here and can be found in reference [5].

The trial Hamiltonian H_t is chosen to be

$$H_t = \sum_{\mathbf{r}} (\nu_{\mathbf{r}} s_{\mathbf{r}} + \eta_{\mathbf{r}} w_{\mathbf{r}}) \tag{7}$$

where $\nu_{\mathbf{r}}$ and $\eta_{\mathbf{r}}$ are variational parameters.

Note that the earlier calculation [1] used a trial Hamiltonian involving both spin and phonon variables with four variational parameters and does not go through the process of obtaining an explicit effective spin Hamiltonian as is done here. After minimising the free energy upper bound with respect to the variational parameters, we obtain results which agree with the previous calculation after subtracting off self-energy terms. The self-energy terms do not appear in the earlier calculation. We have therefore confirmed the results of the earlier calculation with the alternative calculation here.

5. ACKNOWLEDGEMENTS

The authors thank the Malaysian Government and Universiti Sains Malaysia for the Fundamental Research Grant Scheme (FRGS) (Acc. No. 203/PFIZIK/671163) and the Scientific Advancement Grant Allocation (SAGA) Grant No. 304/PFIZIK/635003/A118.

6. REFERENCES

1. P. T. How, B. S. Lee, H. K. Fun, I. A. Razak and S. Chantrapromma, *Phys. Rev.* **2005,** B71, 174109 .
2. A. Usman, S. Chantrapromma and H. K. Fun, *Acta Cryst.* **2001,** C57, 1443.
3. H. K. Fun, B. S. Lee and S. Chantrapromma, *Ferroelectrics.* **2007,** 349, 45.
4. G. A. Jeffrey, *An Introduction to Hydrogen Bonding* . Oxford University Press, New York, **1997.**
5. Mohd Mustaqim Rosli. Study of Hydrogen Bondings in Phenol-Amine Adducts, *M.Sc thesis,* Universiti Sains Malaysia, Penang, Malaysia, **2008.**
6. B. S. Lee, *J. Low Temp. Phys.* **1973,** 13, 81.
7. B. S. Lee, *J. Phys. C.* **1980,** 13, 2651.
8. A. A. Maradudin, E. W. Montroll and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation.* Academic Press, New York, **1971.**