

# Temperature dependence of optical rotation on parity- violating phase transition of D-, L-, and DL-alanine crystals

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# Part I Abstract

- Chirality in Biological System
- Salam Theory: Theory and Supposed Experiment
- Previous Work
- Our Experiment

# Introduction: Chirality

- All biomolecules have to be of one hand, so **homochirality** is a hallmark of life.
- Life is based on L-amino acids and D-sugars rather than the enantiomeric D-amino acids and L-sugars. This broken symmetry is now believed to be a feature of fundamental physics — a result of **symmetry-breaking** by the **weak force**, which makes one enantiomer very slightly more stable than the other.

# Introduction: Salam Phase Transition Theory

- **Salam** postulated that chirality among the twenty amino acids, which make up the proteins, may be a consequence of a **phase transition** which is analogous to that due to **BCS** superconductivity. Salam suggested a unique mechanism whereby the parity violating energy difference (**PVED**) between enantiomers might lead directly to a homochiral product. He surmised that there should exist an abrupt phase transition at a critical temperature  $T_c$ , causing a change in the chirality from D-amino acid to that of more stable “natural” enantiomer, the L-amino acid.

# Introduction: Salam Phase Transition Theory

$$T_c = \frac{\langle \varphi \rangle}{10^3} \exp\left[\frac{-2}{g_{eff} \sigma (1 - 4 \sin^2 \theta)}\right] \approx 2.5 \times 10^2 K$$

# Introduction: Salam Phase Transition Supposed Experiment

1. Measuring differences of **specific heats** .
2. Lower the temperature while measuring the **optical activity** while polarized light is shone upon a particular amino acid crystal. If the polarization vector gets rotated, one may be sure that the appropriate phase transition has taken place.

Salam, A. *Phys Lett B*. **1992**,288,153-160

Salam, A. *J.Mol.Evol.* **1991**,33,105-113

# Introduction: Previous work on this subject

Figureau *et al.* conducted a series of experiments to test the validity of Salam prediction. They observed **no changes** of optical rotation **in solution** after exposing both racemic **DL-cystine and L-cystine** to temperatures ranging from **77K to 0.6K** for three and four days, thus reported **failing to validate** PVED-induced phase transitions predicted by Salam.

Figureau, A.; Duval, E.; Boukenter, A. *Orig. Life. Evol. Biosphere.* **1995**, 25, 211-217

# Introduction: Inaccuracy of previous experiment

- We argue that Figureau samples were taken out of the cryostat after the cooling period, then heated and dissolved in HCl solution at room temperature for measurement. Therefore, their observing no optical rotation in solution only proves that Salam phase transition is **not an irreversible process**,

**But it is not a piece of negative evidence while the transition is reversible.**

**Moreover, their work only denied the configuration change from D-cystine to L-cystine.**



# Experiment: Experiment Design

- In order to study on Salam Phase Transition ( $T_c$  was predicted as about 250K), we have to measure the **optical rotation in crystalline amino acid** while **the temperature is very low**. The variation of optical rotation angle of crystal with temperature is complicated causing by subtle changes in molecular structure e.g. changes of ability of certain groups (such as carboxylate, methyl and amino group) to rotate. The angle depends on chemical bonding and molecular conformation as yet poorly understood way.

# Experiment: Characterization of samples

- The powder of D-alanine, L-alanine and DL-alanine were obtained from Sigma Chemical Co. The amino acids single crystals were well-formed crystals elongated along the *c* axis, which were grown by slow evaporation of saturated aqueous solutions at 4°C, then washed with absolute alcohol, evacuated and kept in a desiccator.

# Experiment: Characterization of samples

- The characterization of D- and L-alanine crystals was performed by **the element analysis** (C, H and N) and **X-ray structure analysis**. It indicates that D-alanine and L-alanine are **pure single crystals** containing **no crystalline water**.

# Experiment: Characterization of samples

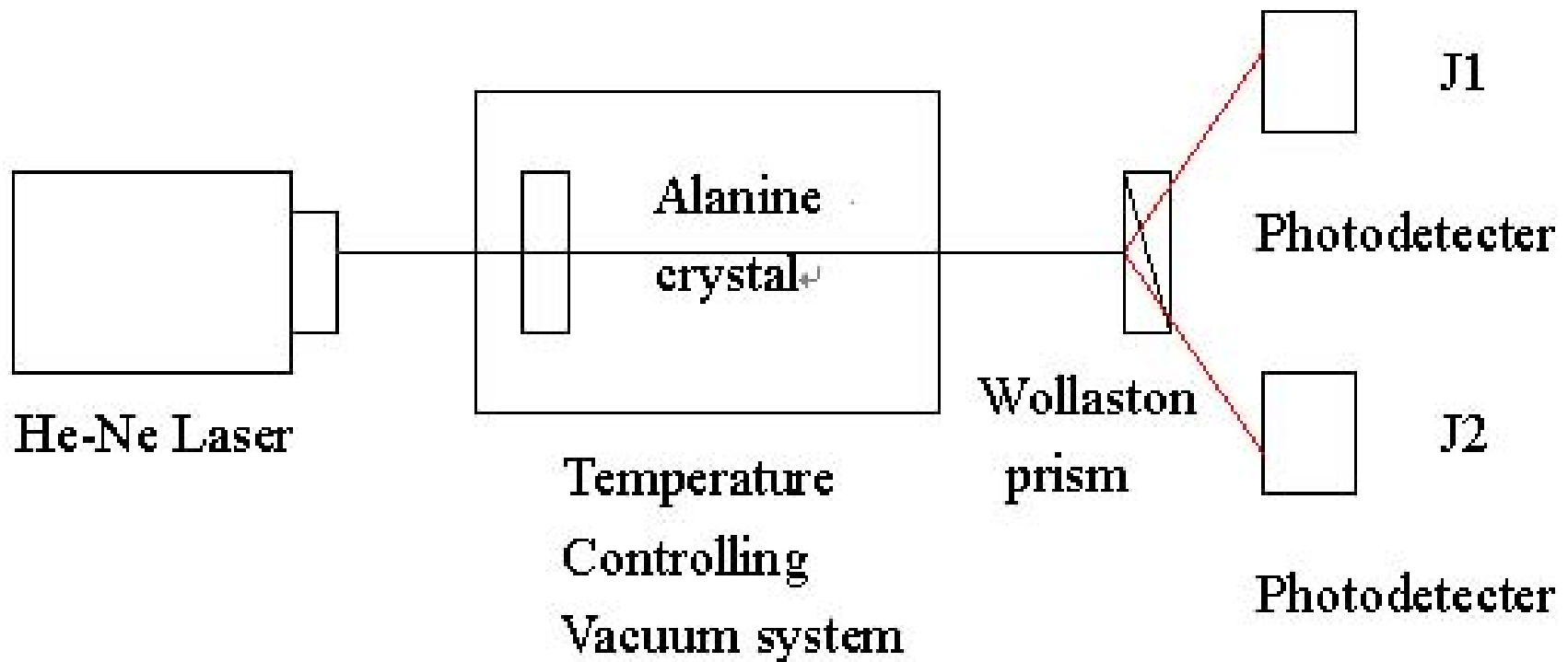
- The crystal structures are orthorhombic with the same space group  $P2_12_12_1$ ,  $Z=4$ , with lattice constants  $a = 0.60388(1), 0.60344(5)$  nm,  $b = 1.23670(3), 1.23668(8)$  nm,  $c = 0.58000(2), 0.57879(3)$  nm of D- and L-alanine (300K),  $\alpha = \beta = \gamma = 90^\circ$ .

# Experiment: Characterization of samples

- The rotation angle  $\zeta$  of the D- and L- alanine solution was measured on **Polarimeter PE-241MC** with the wavelength of 589.6 nm at 293K. By using the formula of  $[\alpha] = \zeta / (L+C)$ , the corresponding  $\alpha$  values of D- and L- alanine were shown to be the same absolute value and of opposite signs.

# Experiment: Apparatus

- Schematic diagram of the apparatus



# Experiment: Measurement

- Linearly polarized light of wavelength 632.8 nm from He-Ne laser source passes through a transparent chiral material of length  $d$  that is located in vacuum temperature-control system. The direct measurement of the polarization direction of a light beam e.g. the rotation signal must be converted into an amplitude signal with the aid of a polarization-optical analyzer. Wollaston prism is a beam splitter that splits the linearly polarized light beam into two component beams polarized normal to each other.

# Experiment: Measurement

- Because the maximum sensitivity and linearity of measurement are obtained by adjusting an angle of  $45^\circ$  between the analyzer and the initial plane of polarization, the component beam intensities  $J_1$  and  $J_2$  are measured with two highly accurate photodetectors by adjusting the transmitting direction of the Wollaston prism to be  $\pm 45^\circ$

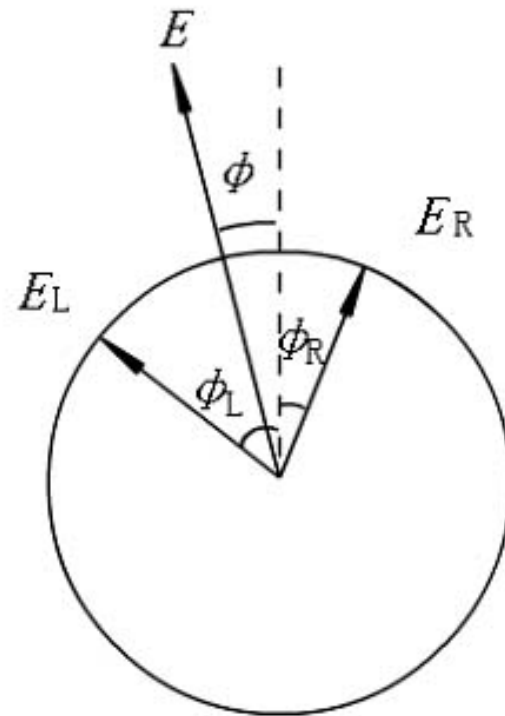
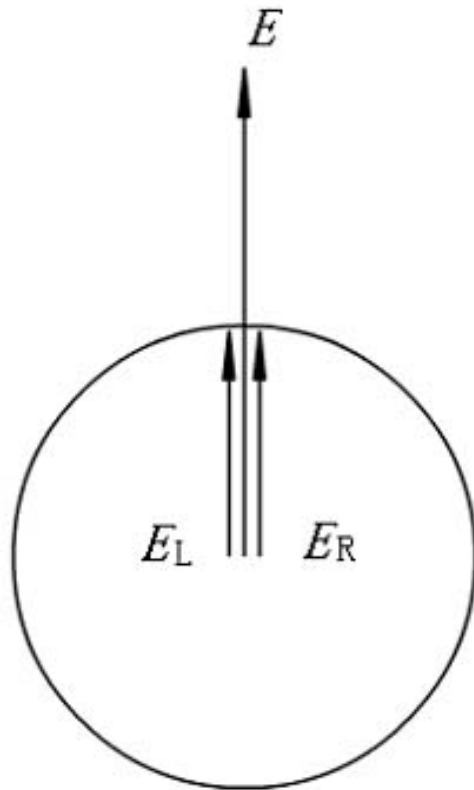


# Experiment: Measurement

- The temperature-dependent optical rotation angles of crystalline DL-alanine, D-alanine and L-alanine have been determined from **230K** to **290K**. The crystals were pre-located in the **temperature-control vacuum sets**, and the beam intensity  $J_1$  and  $J_2$  was measured by two independent highly accurate **photodetectors**.

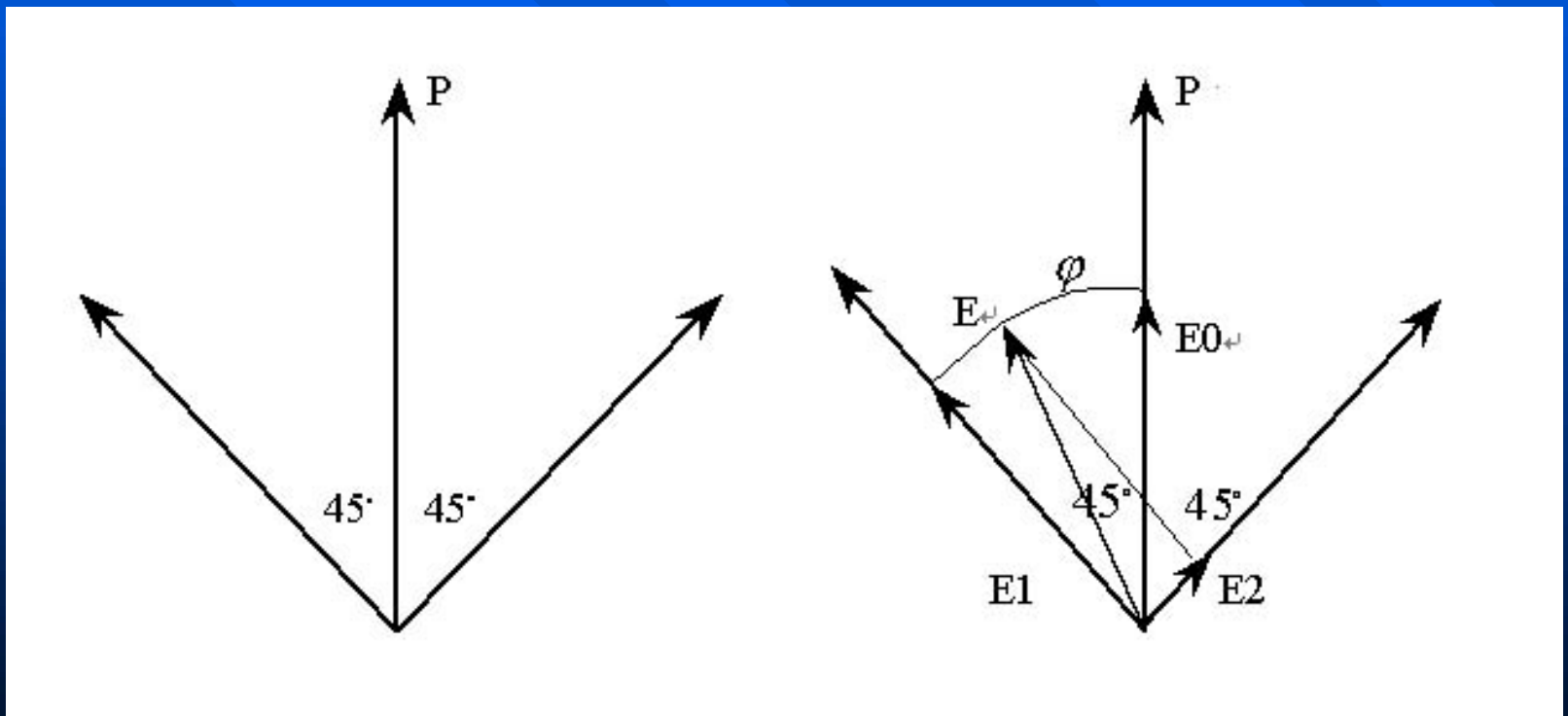
# Experiment: Measurement

- Illustration of optical rotation in chiral material



# Experiment: Measurement

- Resolution of polarization vector through Wollaston prism



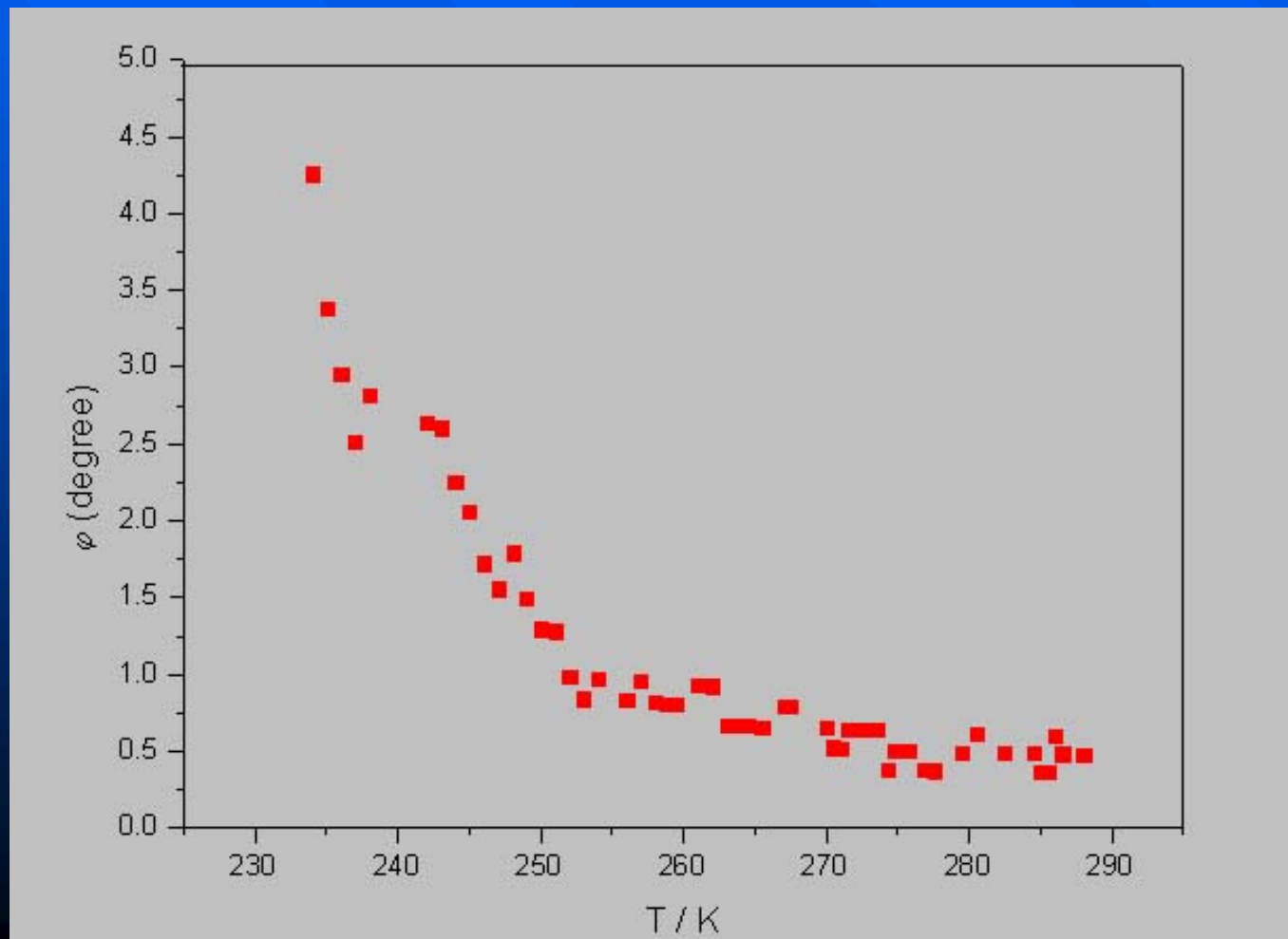
# Experiment: Calculation

- $J_1 = J_0 \cos^2 (45^\circ - \varphi) = J_0 (1 + \sin 2 \varphi) / 2$
- $J_2 = J_0 \cos^2 (45^\circ + \varphi) = J_0 (1 - \sin 2 \varphi) / 2$
- $J_1 - J_2 / J_1 + J_2 = \sin 2 \varphi$
- $\varphi = 1/2 \arcsin (J_1 - J_2 / J_1 + J_2)$

Here  $J_0$  is the intensity in front of the analyzer,  $J_1$  and  $J_2$  is the light intensity behind the analyzer, respectively.

# Experiment: Result- DL\_Ala

Temperature-dependent rotation angle of DL-alanine

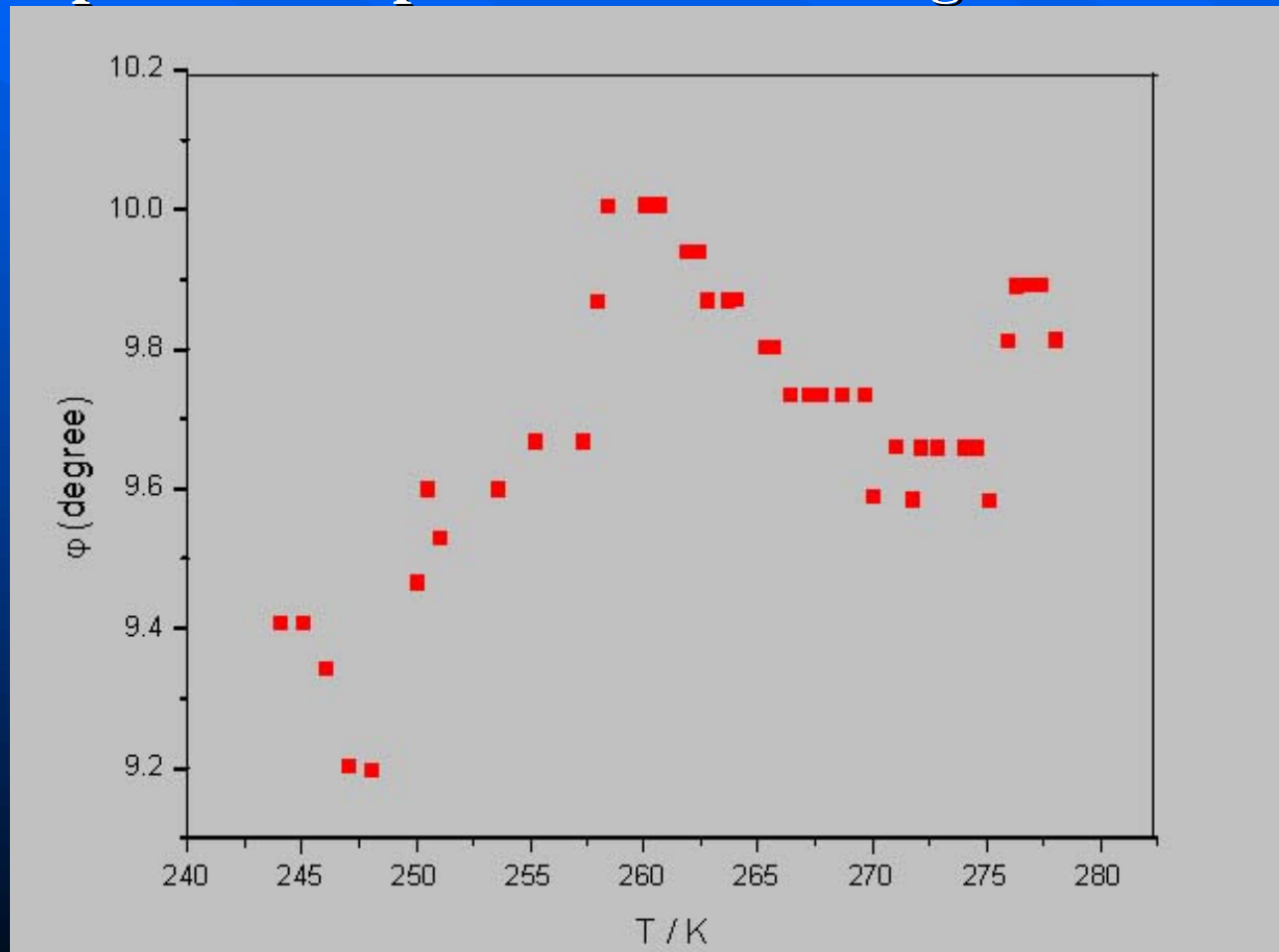


# Experiment: Result- DL\_Ala

- The  $\varphi$  value was equal to  $0.50^\circ \pm 0.10^\circ$  (approach to zero) from 288K to 270K. It proves that DL-alanine is truly **racemic**. When the temperature continuously decreased from 260K through 250K to 234K, the  $\varphi$  value was rapidly increased to  $4.26^\circ$  shown an obvious characteristic variation. According to the Salam prediction, we may be sure that a second order **phase transition** has taken place around  $261 \pm 1$  K.

# Experiment: Result-L\_Al

- Temperature-dependent rotation angle of L-alanine



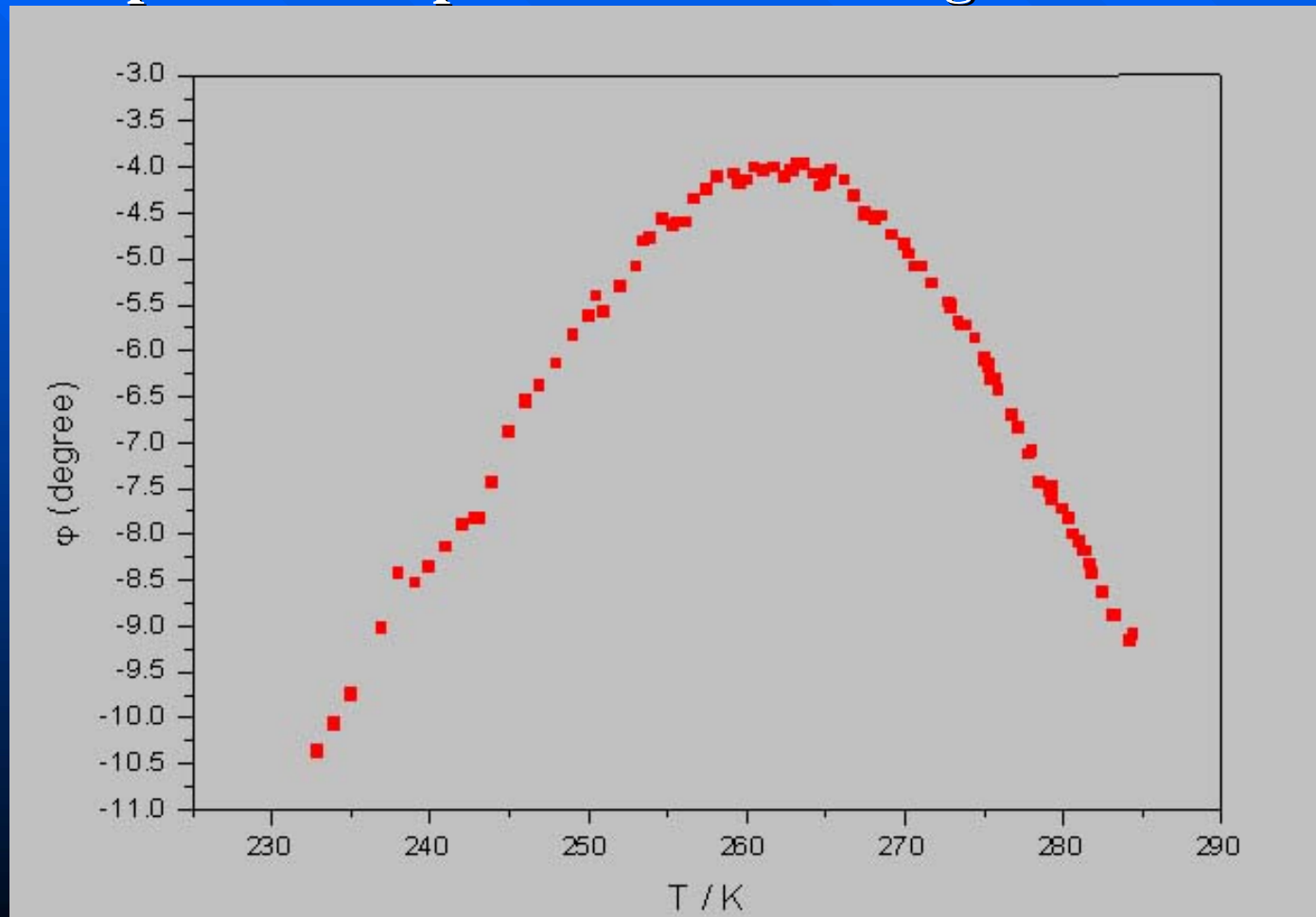
# Experiment: Result-L\_Al

- The  $\varphi$  value was fluctuated in the range of  $9.20^\circ \sim 10.01^\circ$  from 278K to 233K and shown maximum  $10.01^\circ$  at  $260 \pm 1$  K. It coincides a phase transition of lattice mode happened in L-alanine producing a small peak of optical rotation angle.



# Experiment: Result\_D-Ala

- Temperature-dependent rotation angle of D-alanine



# Experiment: Result\_D-Ala

- In contrast, the  $\varphi$  value of D-alanine was obviously increased from  $-9.09^\circ$  (284K) at a maximum  $-3.98^\circ$  (263K) then decreased to  $-10.37^\circ$  (233K) appeared a parabolic reversible transformation.

# Experiment: Result

- It demonstrated that a crucial form of the transition temperature  $T_c$  involved dynamical symmetry breaking. The structures of DL-alanine, D-alanine and L-alanine belong to the orthorhombic system, but the space group is  $P2_12_12_1$  for the D- (or L-) alanine and  $Pna2_1$  for the DL-alanine, respectively. It is reasonable that the optical rotation angle of DL-alanine  $\varphi_{DL}$  is not apparently equal to the sum of D-alanine  $\varphi_D$  plus L-alanine  $\varphi_L$

# Part II Abstract

## Discussion:

- Optical rotation Theory:
  - ✓ Quantum Theory
  - ✓ Freedman Model
- X-ray Diffraction Experiment
- Raman Spectra
- Back to Freedman Model
- New Insight of Salam Theory
- Chemical Evolution of Homochirality

# Discussion: Optical Rotation

- Optical Rotation angle as a probe of molecular chirality :

Based upon the present results we found that a phase transition related with the optical rotation change in D-alanine and DL-alanine is existed as Salam predicted.

# Discussion: Optical Rotation

The rotation of plane-polarized light by chiral molecules arises from the difference in the index of refraction for left and right circularly polarized light. The rotation angle depends on **chemical bonding** and **molecular conformation**.

# Discussion: Optical Rotation

According to Quantum Theory:

The optical rotation parameter  $\alpha, \beta$  is related to the angular frequency of the incident radiation ( $\omega$ ) and the elements of the electric dipole and magnetic dipole, which can be written down as:

$$\alpha = \frac{1}{3\pi\hbar} \sum_j \frac{\omega_{j0} |\langle 0 | \mu | j \rangle|^2}{(\omega_{j0}^2 - \omega^2)}$$

$$\beta = \frac{c}{6\pi^2\hbar} \sum_j \frac{1}{(\omega_{j0}^2 - \omega^2)} \text{Im} \langle 0 | \mu | j \rangle \bullet \langle j | m | 0 \rangle$$

# Discussion: Optical Rotation

- Then we can calculate the rotation angle as :

$$\varphi = \frac{8\pi NL}{3\hbar c} \sum_j \frac{\text{Im} \langle 0 | \mu | j \rangle \cdot \langle j | m | 0 \rangle \omega^2}{(\omega_{j0}^2 - \omega^2)}$$

Here  $|0\rangle$ ,  $|j\rangle$  denotes the ground and excited state wave functions in Dirac presentation, respectively, and  $\omega_{j0} = \omega_j - \omega_0$  is the associated excitation frequency. Here  $\mu$  and  $m$  are the electric and magnetic dipole operators.  $N$  means the total number of atoms in a unit volume.  $L$  denotes the length of light pass,  $\hbar$  is Planck constant and  $c$  is the light velocity.



# Discussion: Optical Rotation

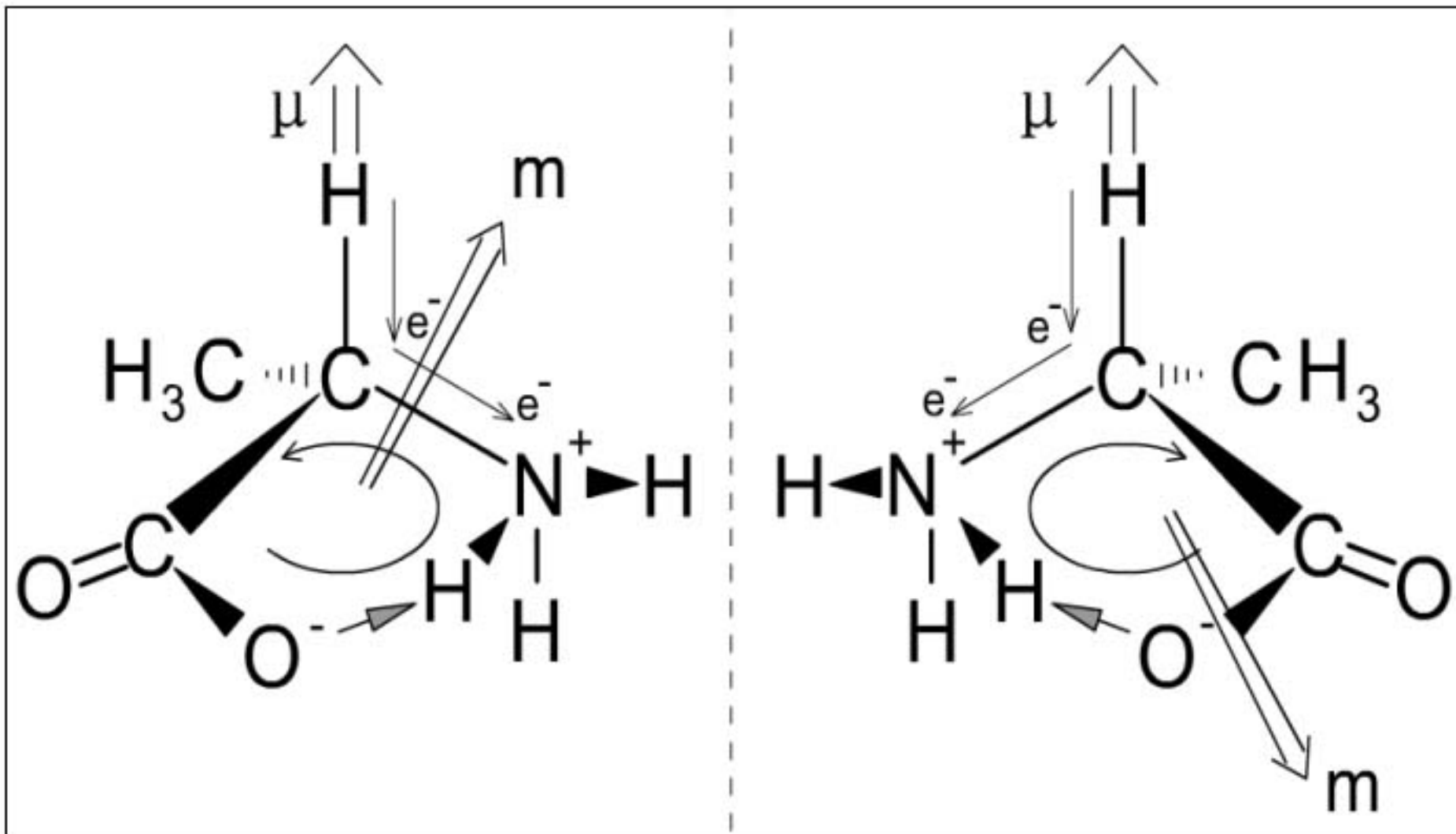
This equation induced by Rosenfeld using quantum mechanics shows that the **interference** of the **electric dipole** and **magnetic dipole** produces the optical rotation effect in optical active medium. To perform this calculation on alanine crystal, not only the contributions of single atoms should be included, but also all the **chemical bonds** and the **molecular conformation** must be considered.

# Discussion: Optical Rotation

## ■ Freedman Model:

T. B. Freedman proposed a model via **vibrationally generated electronic ring currents** to explain the optical rotation effect. In the case of alanine crystal, the  $C_{\alpha}$ -H stretch generates an oscillating electronic current in a molecular ring, adjacent to the methine bond, which is closed by hydrogen bonding. This oscillating ring current gives rise to a large magnetic dipole transition moment.

# Molecular Ring in Alanine



L-alanine

$$\text{Im}(\boldsymbol{\mu} \bullet \boldsymbol{m}) > 0$$

D-alanine

$$\text{Im}(\boldsymbol{\mu} \bullet \boldsymbol{m}) < 0$$

# Discussion: Optical Rotation

- As depicted for the  $C_\alpha$ -H contraction (or lengthening) in D-alanine, positive (or negative) current flowing in the direction  $N \rightarrow C_\alpha$  when electrons are injected into the ring by the  $C_\alpha$ -H contraction (or lengthening), produces a magnetic dipole transition moment,  $m$ , with a component in the direction of the electric dipole transition moment. The rotational strength  $R = \text{Im}(m)$ , is positive (or negative), as observed. The main difference between enantiomers lies in that they produce opposite optical rotation due to the opposite sign of  $\text{Im}(m)$ .

# Discussion: X-ray Diffraction

- In addition to their experiments, a more direct way to testify Salam's phase transition is to conduct temperature-dependent X-ray diffraction or neutron diffraction on alanine enantiomers. **If there is a configuration change of D- to L-, it will be easy to catch this phenomenon for an abrupt change in atom coordinates will be observed.**

# Discussion: X-ray Diffraction

- The data for D-/L- alanine single crystals are listed in Table 1, which are collected at different temperatures on a Siemens R3m/V diffractometer with  $M_o\text{-}K_x$  ( $=0.71073\text{\AA}$ ) radiation. The structure is solved by direct methods and subsequent Fourier Differential Techniques, and refined by full-Matrix least squares using the SHELXTL PLUS program. All non-hydrogen atoms are refined with anisotropic thermal parameters.

# Discussion: X-ray Diffraction

- Dihedral angles was calculated from the atomic coordinates of O(1) O(2) C(1) C(2) H(1) of D- and L-alanine under the temperature dependence of X-ray diffraction data.

# Discussion: X-ray Diffraction Data 300K

Temperature	300K						
Samples	D-Alanine			L-Alanine <sup>Ⓢ</sup>			
Empirical formula	C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>						
Formula weight	89.10						
Crystal system	Orthorhombic						
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>						
Unit cell Dimensions (nm)	a=0.6088(1)			0.60344(5)			
	b=1.2267(3)			1.23668(8)			
	c=0.5800(2)			0.57879(3)			
Volume (nm <sup>3</sup> )	V=0.4331(2)			0.43193(5)			
Z	4						
Atomic coordinates	X	Y	Z	X	Y	Z	
	O(1)	0.7281(2)	0.08438(7)	0.3716(1)	0.7282(1)	0.08437(6)	0.3716(1)
	O(2)	0.4505(2)	0.18519(8)	0.2390(1)	0.4503(1)	0.18512(7)	0.2388(1)
	C(1)	0.4764(2)	0.1611(1)	0.6444(2)	0.4766(2)	0.16118(8)	0.6444(2)
	C(2)	0.5604(2)	0.14163(8)	0.3975(2)	0.5606(2)	0.14163(7)	0.3978(2)
	H(4)	0.441(2)	0.238(1)	0.656(3)	0.440(2)	0.237(1)	0.655(3)
Dihedral angle $\theta$	49.53 °			49.40 °			



# Discussion: X-ray Diffraction Data 270K

Temperature	270K						
Samples	D-Alanine			L-Alanine			
Empirical formula	$C_3 H_7 NO_2$						
Formula weight	89.10						
Crystal system	Orthorhombic						
Space group	$P2_12_12_1$						
Unit cell	a=0.60073(5)			0.60095(5)			
Dimensions (nm)	b=1.23030(7)			1.23388(7)			
	c = 0.57732(4)			0.57904(3)			
Volume (nm <sup>3</sup> )	V=0.42669(5)			0.42936(5)			
Z	4						
Atomic coordinates	X	Y	Z	X	Y	Z	
	O(1)	0.7280(1)	0.08419(6)	0.3723(1)	0.7279(1)	0.08414(6)	0.3725(1)
	O(2)	0.4488(1)	0.18497(6)	0.2388(1)	0.4489(1)	0.18494(6)	0.2388(1)
	C(1)	0.4744(2)	0.16118(8)	0.6442(2)	0.4746(2)	0.16115(8)	0.6445(2)
	C(2)	0.5591(2)	0.14146(7)	0.3978(1)	0.5593(2)	0.14146(7)	0.3980(2)
	H(4)	0.441(2)	0.237(1)	0.656(2)	0.440(2)	0.238(1)	0.656(2)
Dihedral angle $\theta$	45.52°			45.20°			

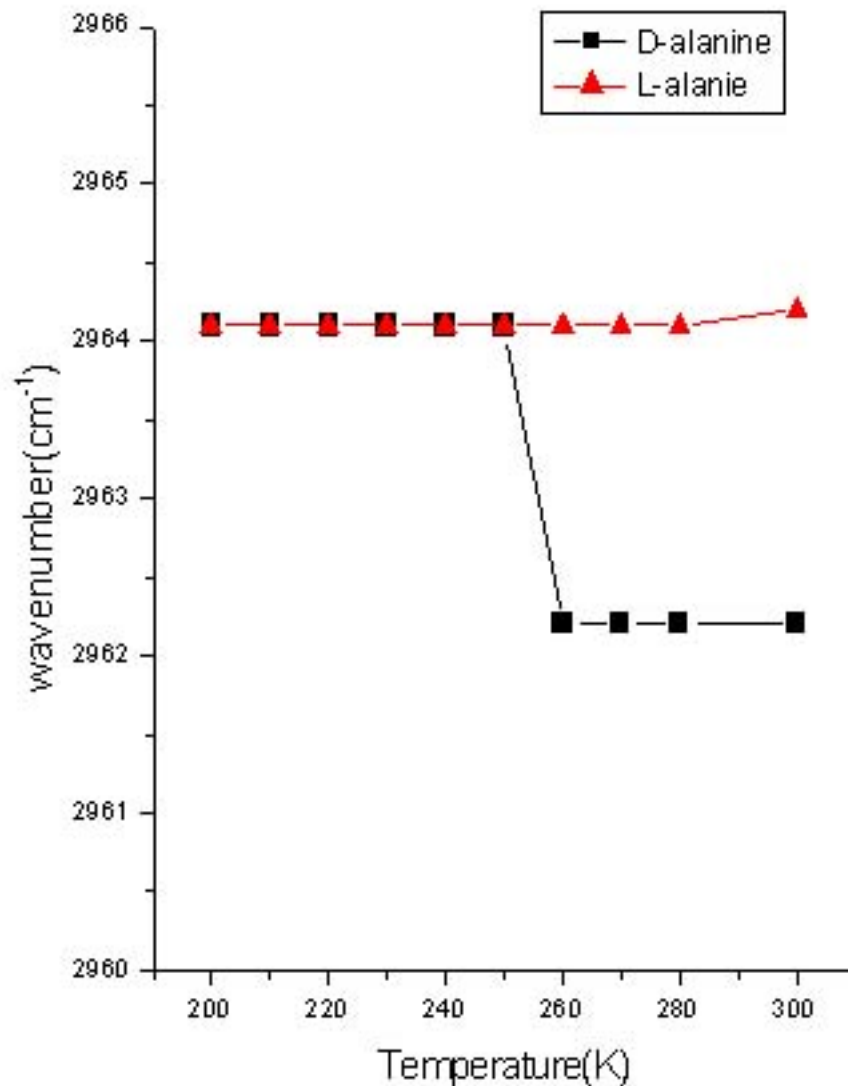
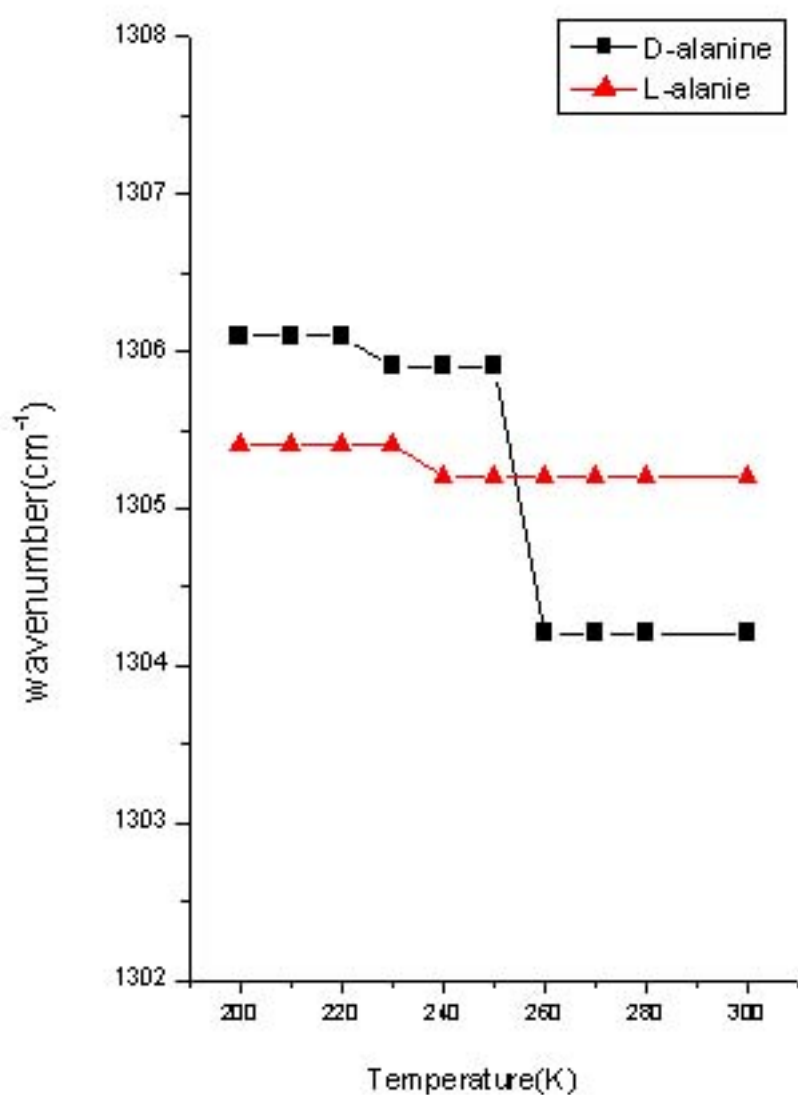
# Discussion: X-ray Diffraction Data 250K

Temperature	250K <sup>a</sup>						
Samples	D-Alanine			L-Alanine <sup>a</sup>			
Empirical formula	C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>						
Formula weight	89.10						
Crystal system	Orthorhombic						
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>						
Unit cell	a=0.60041(3)			0.60002(4)			
Dimensions (nm)	b=1.23179(5)			1.23293(6)			
	c=0.57892(3)			0.57822(2)			
Volume (nm <sup>3</sup> )	V=0.42815(3)			0.42775(4)			
Z	4						
Atomic coordinates	X	Y	Z	X	Y	Z	
	O(1)	0.7282(1)	0.08412(6)	0.3727(1)	0.7279(1)	0.08404(6)	0.3730(1)
	O(2)	0.4481(1)	0.18482(6)	0.2388(1)	0.4480(1)	0.18484(6)	0.2387(1)
	C(1)	0.4734(2)	0.16125(8)	0.6443(2)	0.4736(2)	0.16115(8)	0.6447(2)
	C(2)	0.5582(2)	0.14134(7)	0.3980(1)	0.5587(2)	0.14139(7)	0.3984(1)
	H(4)	0.437(2)	0.237(1)	0.653(2) <sup>a</sup>	0.440(2)	0.237(1)	0.658(2)
Dihedral angle $\theta$	<b>43.97°</b>			<b>45.72°</b>			

# Discussion: Raman Spectra

- Vibration spectra of D- and L-alanine single crystals were measured by Raman spectroscopy from 200K to 300K. A further observation of this phase transition in D-alanine by Raman spectra shows that when temperature exceeds the transition temperature  $T_c$ , the spectra of  $C_\alpha$ -H modes at  $1305\text{cm}^{-1}$  ( $C_\alpha$ -H bending),  $2964\text{ cm}^{-1}$  ( $C_\alpha$ -H stretching) of D-alanine show a variation in its peak positions and relative intensity. As temperature exceeds  $T_c$ , these two peaks show a downward shift of about  $2\text{ cm}^{-1}$  (above  $1\text{ cm}^{-1}$  spectral resolution) on Ranishow 1000 Micro-Raman system.

# Discussion: Raman Spectra



# Discussion: Raman Spectra

- Raman spectra confirm the existence of phase transition of D-alanine crystal. Since the vibrational frequencies of  $C_{\alpha}$ -H bending and stretching modes are very sensitive to the change of electric dipole moment  $\mu$ .

# Discussion: Raman Spectra

- This Raman spectra study indicates the difference of the electric dipole moment  $\mu$  between two enantiomers when temperature is below 250K. This result is of great importance to the understanding of our temperature-dependent optical rotation measurement result.

# Discussion: Optical Rotation

- Raman spectra have confirmed that the phase transition can induce a **change in the electric dipole moment  $\mu$** .
- In addition, the slight variation of atoms' position and a **change of dihedral angle ( $45.32^\circ \rightarrow 43.97^\circ$ )**, which will bring the change in the **magnetic dipole moment  $m$** .

# Discussion: Optical Rotation

- Since  $n$  and  $m$  all undergo a change in their magnitude, it is natural to observe the variation of rotation angle in this phase transition because it is closely related to

$$\text{Im}(\mu \cdot m)$$



# Discussion: Optical Rotation

- From Freedman's model, we can make a sound explanation of the phenomenon observed in our experiments. **The existence of the phase transition suggested by Salam is verified by our experiments.** However, his suggestion that this **phase transition will eventually change D-alanine to L-alanine is denied.** What we intend to emphasize here is the variation of rotation angle can not be simply and solely interpreted as the configuration change of  $D \rightarrow L$ . As we have already presented, the optical rotation is closely related to  $\text{Im}(\mu \cdot m)$ , so **changes of magnitude of  $\text{Im}(\mu \cdot m)$  will also bring about this phenomenon.**

# Discussion: New insight of Salam theory

- Our series of experiments confirm the existence of a phase transition in amino acids. Although Salam's hypothesis has failed to explain homochirality only via this phase transition, the significance of the different behavior between D- and L- amino acids in the phase transition will never be ignored.

# Discussion: New insight of Salam theory

- The parity violation effect in weak interaction has made enantiomers different. Berger and Quack's study in a detailed analysis of dynamic chirality proved that the dihedral angle between the O<sub>2</sub>C and C-H planes plays an important role in determining the intrinsic energies of the alanine molecules and this difference has been used in the calculation of Parity Violating Energy Difference (PVED).

# Discussion: New insight of Salam theory

- According to Quack's theoretical method by means of highest level ab initio studies (MC-LR), the PVED value is  $1.2 \times 10^{-19}$  Hartree ( $3.3 \times 10^{-18}$  eV/molecule), namely L-alanine is more stable than D-alanine. D-alanine and L-alanine have shown obvious difference at 250K. Quack has also proved that the difference between enantiomers induced by weak neutral currents is too minor to be detected by experimental methods under normal conditions.

# Discussion: New insight of Salam theory

- But as we have already illustrated, D-, L-, and DL-alanine crystals display distinct behavior in all experimental methods in the specific phase transition process. A possible explanation could be: the minor difference between D- and L-enantiomers (PVED: about  $10^{-18}$  -  $10^{-17}$  eV) has been enlarged to a detective level during this phase transition due to quantum mechanical cooperative and condensation phenomena. This amplified energy difference will become the foundation of later amplification mechanism.

# Discussion: New insight of Salam theory

- Significantly, the biological system when homochirality was achieved meets well the formation requirements of a dissipative structure — the critical transition point is far from equilibrium; the control parameter PVED, whose value determines the probability of Salam phase transition, has a transition threshold; the occurrence of Salam phase transition will in turn enlarge PVED nonlinearly.

# Discussion: New insight of Salam theory

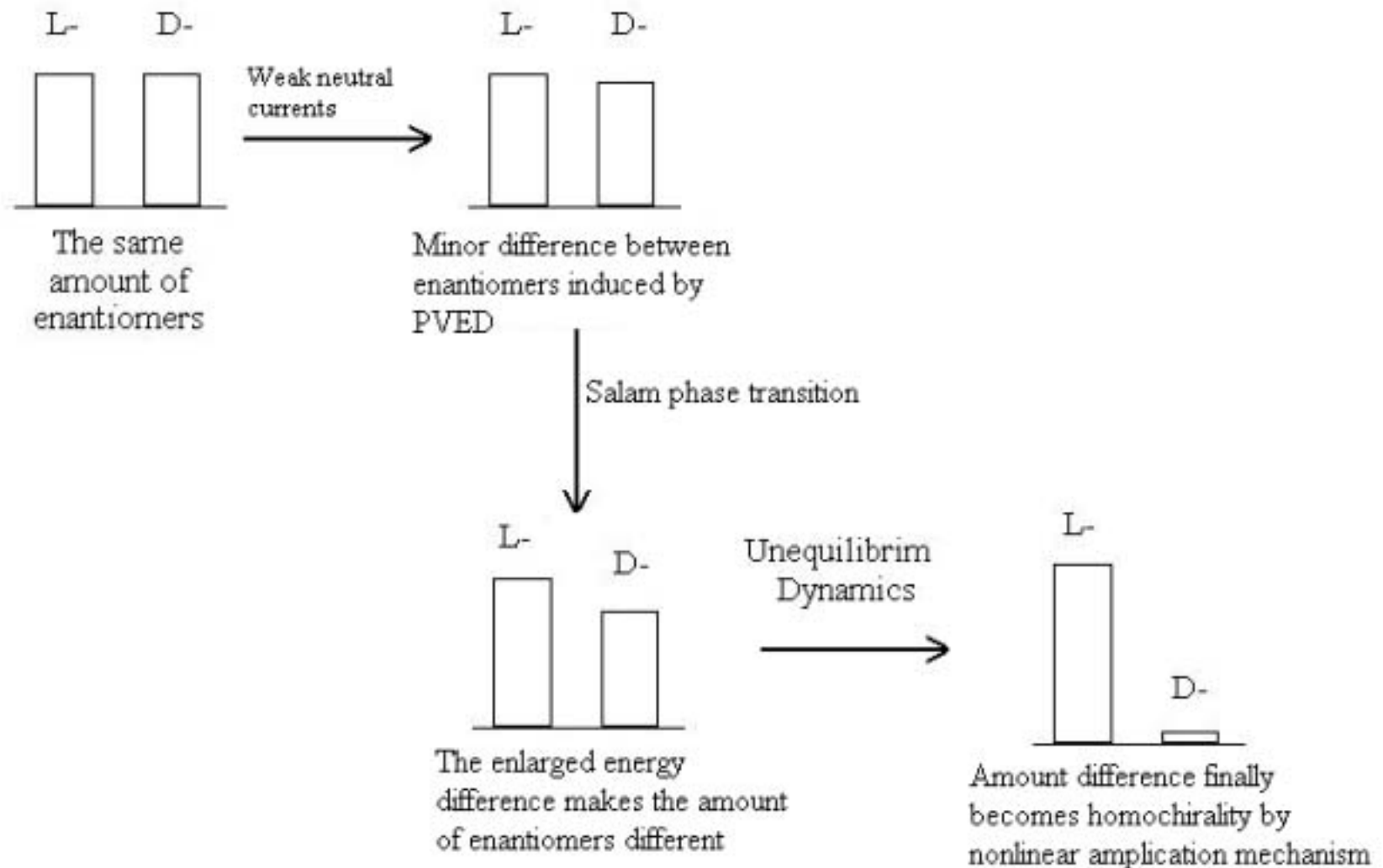
- Hence, if the temperature is kept in the transition temperature range all along, the control parameter PVED can exceed its critical value (threshold) for enough time, and it is possible to form a dissipative structure and finally develop into an ordered and homochiral system. This scenario is being tested in our laboratory.

# Discussion: New insight of Salam theory

- At last, we emphasize again the significance of Salam phase transition in the evolution of homochirality: instead of an ultimate solution to the problem, it actually plays as a first step of amplification mechanism. It connects the microcosmic difference (PVED) between biomolecular enantiomers with nonlinear process in a macrocosmic biological system.



# Chemical evolution of homochirality



**Thanks**