Parity Violations on Molecular Chirality: Neutron Crystal-Structure of D- and L-alanine^{*}

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Abstract The role of chirality determines the origin of life that almost all amino acids utilized in living systems are of the L-type. Starting from Z^0 interactions, Salam speculated on an explanation in terms of quantum mechanical cooperative and condensation phenomena where the electron-nucleon system has the same status as Cooper-pairing, which could give rise to second-order phase transitions (including D to L transformations) below a critical temperature T_c (~ 250 K). Neutron diffraction of single crystal D- and L-alanine was performed to look for the characteristic structural feature above and below the T_c (295 K and 60 K) and the possibility of D- to L-type transformation. Data analysis of the temperature effect on the crystal lattice together with the NH_3^+ torsional motion, parity-violating energy difference (ΔE_{PV}) as a function of dihedral angle (ω), the CO_2 (θ) and NH_3 (ψ) torsion angles and the contribution of $\text{C}_\alpha - \text{H} \cdots \text{O} = \text{C}$ hydrogen bond is discussed. Observation of the behavior of weak hydrogen bonding during the cooling process threw a light on the distinction between D- and L-alanine, which could be attributed to the parity-violating weak interactions. Measurements of the neutron crystal-structure of D-alanine rule out the possibility of configuration transition to L-alanine, which means that Salam phase transition is not a conventional structure transition.

Keywords: Parity violation, Molecular chirality, Neutron diffraction, D- and L-alanine

1 Introduction

The major constituents of biological molecules, such as amino acids which contain carbon, oxygen, nitrogen and hydrogen, are less than 0.4 nm in diameter. The behavior of small molecules is a reflection of the intrinsic properties of the constituent atoms. Hence, it might be expected that the behavior of large macromolecules can be explained by a knowledge of atomic properties. Salam^[1-3] started with the possibility of defining a science of life on atomic physics. Based on the theory of the parity-violating electroweak interaction, he suggested that chirality among the twenty amino acids which make up the proteins may be a consequence of a second order phase transition below a critical temperature, which is analogous to that due to BCS superconductivity. A crucial form for the transition temperature involves symmetry breaking. By using Ginzburg-Landau equation, the T_c is presented.

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

Where $\langle \varphi \rangle$ is expressed as a complex auxiliary Higgs scalar field; θ is the Weinberg angle; g_{eff} is an attractive coupling constant between spin up ($\uparrow$) and spin down ($\downarrow$) electrons and antielectrons. Assuming that $\sigma(0) = m_Z^2$, then $g_{\text{eff}} \sigma(0) \approx 1$. The sign of g_{eff} is part of the assumption of the Hamiltonian which signifies an attractive force between Cooper-paired systems of electrons consisting of one of the particles replaced by its antiparticle with a factor of two which appears in the mass term. The elemental idea of Salam is that a similar formula may hold for the case of amino acid chains in protein. The peptide bond which gives rise to proteins could be reduced to the simple form

Salam assumed the mechanism that the hydrogens ($\text{H} - \text{C}_\alpha$ and $\text{N} - \text{H}$) give up loose electrons and act as metallic hydrogens. He conjectured the analogy of the "superfluidity" exhibited by

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amino acids is to “superfluidity” in superconductors. The “superfluidity” phenomena of amino acids can be measured by shining on these external light sources. He suggested two direct ways, one is to lower the temperature while measuring the optical activity, the second is by measuring differences of specific heats and looking for anomalies in the curve of C_p versus T , for evidence of his hypothesis^[3].

We have performed six kinds of experiments to verify the parity violation of the electroweak force on the phase transition of single crystals of D- and L-alanine (valine). An obvious phase transition was shown in specific heat discontinuity at T_c by the differential scanning calorimetry (DSC), existed in both the D- and L-valine(alanine)^[4-5]. The differential peak of specific heat discontinuity was shown to be on the order $6.2 \times 10^{-5} \text{ eV} \cdot \text{molecule}^{-1} \cdot \text{K}^{-1}$ at T_c , with the biologically dominant L-valine found to have lower energy^[6]. Recently, Barthes *et al.*^[7] found the small jump in the DSC curve of L-alanine in the 240 ~ 250 K temperature range. It was also confirmed by the observation of a large anomaly of the ultrasound attenuation at 247 K^[8]. DC-magnetisation measurements on a SQUAD showed a difference in the magnetic susceptibility (χ_p) as a function of temperature between the D- and L-alanine, while the temperature varies in the range of 200 ~ 250 K, χ_p values of D- and L-alanine are nearly opposite. This gives some clues for the WNC (weak neutral current) playing a contrary parity-violation role in the magnetic behavior of D- and L-alanine molecules at this temperature range^[9]. Laser Raman spectra of D- and L-alanine showed that when the temperature exceeds the transition T_c ($\approx 250 \text{ K}$), the spectra of $C_\alpha - \text{H}$ modes at 1305 cm^{-1} ($C_\alpha - \text{H}$ bending), 2964 cm^{-1} ($C_\alpha - \text{H}$ stretching) of D-alanine show an obvious variation in its peak positions. These two peaks show a wavenumber shift of about 1.7 cm^{-1} , which is 1 cm^{-1} above the spectral resolution. Raman spectra confirmed the existence of phase transition of D-alanine crystal around 250 K ^[9]. ^1H MAS (magic-angle spinning) ssNMR spectra of D-alanine showed an obvious upshielding of the $^1\text{H} - C_\alpha$ from 290 K to 220 K. The integral peak area ratio of NH_3^+ , $C_\alpha - \text{H}$ and the CH_3 group in D-alanine was gradually moved from 3 : 1 : 3 to 3 : 0 : 4^[10], presented the tendency of metallic behavior of H_α . Very recently, we have measured successfully the temperature dependence of the natural optical rotation in biaxial crystal of monoclinic valine (DL-, D- and L-type)^[11]. The results provide a direct evidence of Salam hypothesis. All of these observations have been discussed with

respect to their possible relevance of the Z^0 force of Salam's putative phase transition in the origin of homochirality. The aim of the present study is to look for the characteristic structure feature of the phase transition including the possibility of the D- to L-type transformation.

2 Experimental

D- and L-alanines were purchased from Sigma Chemical Corporation. The single crystals were grown by slow evaporation from a methanol/water solution, and were of dimensions $7 \text{ mm} \times 4 \text{ mm} \times 1.5 \text{ mm}$ (D-alanine) and $4 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}$ (L-alanine), prepared by M. Ghosh and used in neutron diffraction. The other sets of D-alanine ($1.00 \text{ mm} \times 1.00 \text{ mm} \times 0.70 \text{ mm}$) and L-alanine ($0.30 \text{ mm} \times 0.40 \text{ mm} \times 0.50 \text{ mm}$) prepared by Y. Gong and used in X-ray diffraction, respectively.

The crystal structure of L-alanine, $\text{C}_3\text{H}_7\text{O}_2\text{N}$, has been determined from copper X-radiation by Simpson^[12] at 298 K and from Mo- K_α radiation by Destro^[13] at 23 K. Lehmann *et al.*^[14] have performed the neutron diffraction of L-alanine at 298 K. We have determined the crystal structure of D- and L-alanine at 300 K, 270 K, 250 K on a Rigaku RAXIS-RAPID imaging plate diffractometer by Mo- K_α X-radiation^[9], which showed no obvious change in C-H bond lengths as a function of temperature to be taken as the structural evidence of geometrical changes. We have extended this work to include a neutron diffraction study of both the D- and L-alanine above and below the critical temperature (295 K and 60 K). In this way we hope to be able to observe any geometric changes involving the $C_\alpha - \text{H}$ and N-H hydrogen bond lengths to which neutron diffraction will be particularly sensitive. Our work will also allow a direct comparison between the D- and L-alanine crystal structures.

The neutron source at ISIS for beam time was applied to do the neutron diffraction of D- and L-alanine single crystals on 5 April 2001. The data were collected by Chick C. Wilson in ISIS facility of CLRC Rutherford Appleton Laboratory. The resulting structure of L-alanine is shown in Fig. 1.

3 Results and discussion

The present refined structure of L-alanine at 295 K is in agreement with the Lehmann's results^[14]. The basic features of both the D- and L-alanine between 295 K and 60 K are shown by not only the natural reduction of the ADPs (atomic displacement parameters) but also some unusual structural properties.

Fig. 1 Structure of L-alanine determined by neutron diffraction

3.1 Temperature-dependent variation of parameters a , b , c (crystal lattice distortion)

The crystal structure of L-alanine has been given. From copper X-radiation the unit cell dimensions are $a = 0.6032$ nm, $b = 1.2343$ nm, $c = 0.5784$ nm at 298 K^[12]. Low temperature X-ray diffraction results at 23 K are $a = 0.5928$ nm, $b = 1.2260$ nm, $c = 0.5794$ nm^[13]. Neutron diffraction results at 298 K are $a = 0.6025(7)$ nm, $b = 1.2324(14)$ nm, $c = 0.5783(6)$ nm^[14]. The crystals are orthorhombic with space group $P2_12_12_1$. In the present work, the dimensions of the cell of D-/L-alanine are: $a = 0.6025/0.6036$ nm; $b = 1.2324/1.2342$ nm; $c = 0.5783/0.5788$ nm at 295 K and $a = 0.5942/0.5940$ nm; $b = 1.2261/1.2274$ nm; $c = 0.5785/0.5806$ nm at 60 K, respectively. The temperature-dependent variation of parameters a , b and c showed the crystal lattice distortion (Table 1). The parameter a shrank mostly ~ 0.009 nm ($-\Delta a = 0.0083/0.0096$ nm) and the longest side b of the unit cell reduced a smaller amount, ~ 0.0065 nm ($-\Delta b = 0.0063/0.0068$ nm). In contrast to a and b , the parameter c

showed a slight lengthening up to ~ 0.0002 nm ($-\Delta c = 0.0002/0.0018$ nm) i. e. a negative thermal expansion along the c axis. The anomalous increase of the lattice parameter c on cooling could be ascribed to a progressive conformational change of the NH_3^+ group of the zwitterionic molecule^[17]. When the temperature-dependent behavior of a , b and c is known, this can be transformed to the changes in hydrogen bond lengths and angles connected with the torsional barrier. The small difference between alanine enantiomers may result from the parity-violating energy difference, manifested remarkably beneath the critical temperature of phase transition in lattice distortion.

3.2 Temperature dependence of the NH_3^+ torsional motion

The crystalline conformations of D- and L-alanine molecules are in the zwitterionic forms. All the three hydrogen atoms of the ammonium group form hydrogen bonds with other molecules. Two of the hydrogen bonds involve the oxygen atom designated O(2), and one hydrogen bond involves the atom designated O(1). The O(2) has a slightly larger negative charge than O(1). The hydrogen bond O(2) $\cdots$ H(4) links the alanine molecules together to form a chain along the c axis. The other two hydrogen bonds tie these chains into a three dimensional network. The variations of hydrogen bond lengths and angles exhibit temperature-dependence. The lengths of the O(1) $\cdots$ H(1) bond of D- / L-alanine are shortened mostly (0.0023/0.0033 nm), the lengths of the O(2) $\cdots$ H(4) bond are less shortened (0.0001/0.0015 nm) and the O(2) $\cdots$ H(6) bond are shortened (0.0016/0.0011 nm) on cooling. Furthermore, we notice that when the temperature decreases from 295 K to 60 K, the angles N(1) – H(1) $\cdots$ O(1) of D-/L-alanine decrease $0.48^\circ/0.70^\circ$; N(1) – H(4) $\cdots$ O(2) increase $1.65^\circ/$

Table 1 Neutron diffraction data of unit-cell parameters of D- and L-alanine at 295 K and 60 K

T/K	60		295	
Sample	D-alanine	L-alanine	D-alanine	L-alanine
Crystal system	Orthorhombic			
Space group	$P2_12_12_1$			
$\alpha = \beta = \gamma$	90°			
Z	4			
Unit-cell parameters	$a = 0.5942$	0.5940	0.6025	0.6036
(nm)	$b = 1.2261$	1.2274	1.2324	1.2342
	$c = 0.5785$	0.5806	0.5783	0.5788
V/nm^3	0.4215	0.4233	0.4294	0.4312
R indices(all data)	0.0799	0.0588	0.0844	0.0784
No. of refins. used	1968	2023	836	1008
No. of parameters	119	118	119	118

Table 2 Distances (nm) and angles($^{\circ}$) in the hydrogen bonds of D- and L-alanine at 295 K and 60 K

T/K	60		295	
Sample	D-alanine	L-alanine	D-alanine	L-alanine
N(1) – H(6)	0. 1038(4)	0. 1040(3)	0. 1037(7)	0. 1048(8)
H(6)···O(2)	0. 1807	0. 1808	0. 1823	0. 1819
N(1)···O(2)	0. 2815	0. 2818	0. 2831	0. 2836
$\angle$ N(1) – H(6)···O(2)	162. 62	162. 47	163. 18	162. 24
N(1) – H(4)	0. 1050(4)	0. 1059(3)	0. 1071(8)	0. 1054(5)
H(4)···O(2)	0. 1751	0. 1751	0. 1752	0. 1766
N(1)···O(2)	0. 2791	0. 2799	0. 2809	0. 2808
$\angle$ N(1) – H(4)···O(2)	169. 78	169. 07	168. 13	168. 65
N(1) – H(1)	0. 1036(4)	0. 1045(3)	0. 1031(7)	0. 1033(6)
H(1)···O(1)	0. 1832	0. 1828	0. 1855	0. 1861
N(1)···O(1)	0. 2834	0. 2838	0. 2855	0. 2861
$\angle$ N(1) – H(1)···O(1)	161. 82	161. 33	162. 30	162. 03

^{*} $\text{N}(1) - \text{H}(6) \cdots \text{O}(2) [x + 1/2, -y + 1/2, -z - 1]$; ^{*} $\text{N}(1) - \text{H}(4) \cdots \text{O}(2) [x, y, z - 1]$; ^{*} $\text{N}(1) - \text{H}(1) \cdots \text{O}(1) [-x - 1/2,$

$-y, z - 1/2]$; ^{*}The values for the heavy-heavy bond lengths are corrected for thermal motion effects (using the TLS method).

0. 42 $^{\circ}$. However, the angle N(1) – H(6) ···O(2) of D-alanine shows the opposite behavior with L-counterpart, 0. 56 $^{\circ}$ decrease for D-alanine and 0. 23 $^{\circ}$ increase for L-alanine(Table 2).

What is the driving force for the torsional motion of NH_3^+ group on cooling? Barthes *et al.*^[7] explained that according to the Jahn-Teller theorem^[15], any non-linear molecular system in a degenerate electronic state is unstable and will undergo a distortion to form a system of lower symmetry and lower energy, thereby lifting the degeneracy. In the L-alanine molecule, the charged NH_3^+ rotator is of C_{3v} symmetry, with a degenerate fundamental level. Two types of eigenfunctions are found, a state with nuclear spin 3/2, and E-states with nuclear spin 1/2. In analogy with a dynamic Jahn-Teller interaction, the E-states

of NH_3^+ may couple with some lattice vibrations of appropriate symmetry. In this assumption, the NH_3^+ group could undergo simultaneously a dynamic distortion and a lifting of the degeneracy of its group and excited states. Hence, the alanine structure could become frustrated on cooling under the opposite influence of competing interactions: the crystal packing forces and the charge-phonon coupling on the other hand. The increase of c on cooling is an attempt to relax the increasing opposite stresses and also reflects the intrinsically different spin properties on the spin-phonon coupling between D- and L-alanine.

3.3 Parity-violating energy difference (E_{PV}) as a function of dihedral angle (α)

The parity violation of WNC between an electron and a

Table 3 Dihedral angles $\alpha(^{\circ})$ of D- and L-alanine at 295 K and 60 K

T/K		60				
Sample		D-alanine			L-alanine	
Atomic coordinates	X	Y	Z	X	Y	Z
O(1)	0. 272821	− 0. 083928	0. 374374	− 0. 273424	0. 083680	− 0. 375195
O(2)	0. 557971	− 0. 184410	0. 238593	− 0. 559147	0. 184060	− 0. 238903
C(1)	0. 445283	− 0. 140902	0. 399543	− 0. 445737	0. 140732	− 0. 400237
C(2)	0. 533045	− 0. 161241	0. 645476	− 0. 533363	0. 161032	− 0. 645747
H(2)	0. 575140	− 0. 248207	0. 660504	− 0. 575046	0. 247766	− 0. 662025
Dihedral angle α		45. 08(1)			45. 49(1)	

T/K		295				
Sample		D-alanine			L-alanine	
Atomic coordinates	X	Y	Z	X	Y	Z
O(1)	0. 270747	− 0. 084793	0. 371340	− 0. 272045	0. 084890	− 0. 370967
O(2)	0. 550251	− 0. 185016	0. 238076	− 0. 549323	0. 185229	− 0. 238593
C(1)	0. 439673	− 0. 141230	0. 397257	− 0. 439420	0. 141562	− 0. 398516
C(2)	0. 523071	− 0. 161352	0. 643710	− 0. 523602	0. 161327	− 0. 644605
H(2)	0. 564254	− 0. 247800	0. 658568	− 0. 561385	0. 247275	− 0. 661849
Dihedral angle α		44. 37(1)			45. 75(1)

Fig. 2 Parity-violating potential as a function of the orientation of the carboxylate group of zwitterionic L-alanine obtained with the 6-31G basis set^[21]

nucleon causes an energy difference between mirror image molecules^[16] through the spin-orbit coupling^[17-18]. Although this energy difference is very small, it can be the origin of the ubiquity of L-amino acids and D-sugars in the biochemistry of living organisms. By early theoretical quantitative calculation based on SDE-RHF, it has been claimed that L-amino acids are more stable than their D-counterparts^[19-20].

Berger and Quack^[21] performed a systematic study on the role of the conformation of the carboxylate group and used a multi-configuration self-consistent reaction field (MCSCRF) to study the parity-violating effects in the zwitterionic structure of L-alanine. They displayed the parity-violating potential E_{PV} as a function of the conformational dihedral angle (α) of the carboxylate plane with respect to the $C_\alpha - CO_2 - H_\alpha$ plane, obtained with the 6-31 + G^* basis set. They found that the sign of E_{PV} changed from negative (namely, L-alanine is more stable than the D-alanine) to positive values (that is, D-alanine is stabilized) through the range between 0° and 360° . In the present study, the dihedral angles (α) of D- and L-alanine calculated from neutron diffraction were 45.079° (60 K), 44.373° (295 K) (D-alanine) and 45.489° (60 K), 45.748° (295 K) (L-alanine), respectively (Table 3). The dihedral angles of zwitterionic L-alanine at 60 K and 295 K drop into the region of $\alpha < 60^\circ$ (Fig. 2). In this region E_{PV} is actually negative values, namely, L-alanine is more stable than

Fig. 3 Definition of two torsion angles of the L-alanine zwitterions

Table 4 CO_2 (θ) and NH_3 (ψ) torsion angles of D- and L-alanine

T/K	60		295	
	D-Ala	L-Ala	D-Ala	L-Ala
$\theta(N-C-C-O^1)$	$18.13(1)^\circ$	$-18.31(1)^\circ$	$18.13(1)^\circ$	$-18.79(1)^\circ$
$\psi(H^1-N-C-C)$	$58.16(1)^\circ$	$58.03(1)^\circ$	$58.68(1)^\circ$	$58.97(1)^\circ$

D-alanine.

3.4 Parity-violating energy as a function of NH_3 (ψ) and CO_2 (θ) torsion angles

The magnitude and sign of E_{PV} value of amino acids are very sensitive to the conformation of the molecule^[22-23]. Kikuchi *et al.*^[24] used the spin-orbit coupling SCF (SOC-SCF) wavefunction on the basis of Breit-Pauli Hamiltonian and generalized spin-orbitals to calculate the parity-violating energy of chiral alanine. The conformation of zwitterionic structure of L-alanine(L-ALAZ) was characterized by two torsion angles: ψ defines the NH_3 conformation and θ defines the CO_2 conformation (Fig. 3). The E_{PV} values depend largely on the rotation angle θ and ψ while the effect of the CH_3 group on the electronic structure is small. Energy map was calculated by the SOC-SCF GB method with the $[5s2p/3s]$ basis set as a function of the NH_3 (ψ) and CO_2 (θ) torsion angles (Table 4). The E_{PV} values overturn sign from -4.8×10^{-20} to $+7.1 \times 10^{-20}$ hartree in the (θ , ψ) conformational space. In the present study, the torsion angles of CO_2 (θ) and NH_3 (ψ) for L-ALAZ are approximately -18.5° and 58.5° respectively. In this specific conformation, E_{PV} value is located at the negative part of the energy map, which means that L-ALAZ is more stable than its counterpart (Fig. 4).

Fig. 4 The E_{PV} energy map of L-alanine zwitterions in aqueous solution calculated by the SOC-SCF-GB method with the $[5s2p/3s]$ basis set as a function of the NH_3 (ψ) and CO_2 (θ) torsion angles^[24]

Table 5 Neutron diffraction data of bond lengths(nm) of D- and L-alanine

T/K	60		295	
Bond	D-Ala	L-Ala	D-Ala	L-Ala
C(1) – O(1)	0. 1249(1), 0. 1251 *	0. 1249(2), 0. 1251 *	0. 1245(4), 0. 1252 *	0. 1239(4), 0. 1246 *
C(1) – O(2)	0. 1265(2), 0. 1267 *	0. 1270(1), 0. 1272 *	0. 1259(5), 0. 1265 *	0. 1260(3), 0. 1266 *
C _α (2) – C(1)	0. 1536(2), 0. 1537 *	0. 1538(1), 0. 1539 *	0. 1532(4), 0. 1537 *	0. 1532(2), 0. 1537 *
C _α (2) – N(1)	0. 1491(1), 0. 1493 *	0. 1490(1), 0. 1492 *	0. 1491(3), 0. 1499 *	0. 1484(3), 0. 1492 *
C _α (2) – C(3)	0. 1525(2), 0. 1528 *	0. 1529(1), 0. 1531 *	0. 1525(4), 0. 1535 *	0. 1525(4), 0. 1535 *
N(1) – H(1)	0. 1036(4)	0. 1045(3)	0. 1031(7)	0. 1033(6)
N(1) – H(4)	0. 1050(4)	0. 1059(3)	0. 1071(8)	0. 1054(5)
N(1) – H(6)	0. 1038(4)	0. 1040(3)	0. 1036(7)	0. 1048(8)
C _α (2) – H _α (2)	0. 1099(4)	0. 1097(3)	0. 1098(8)	0. 1090(5)
C(3) – H(3)	0. 1086(6)	0. 1097(4)	0. 1114(10)	0. 1085(8)
C(3) – H(5)	0. 1092(5)	0. 1095(4)	0. 1095(11)	0. 1092(11)
C(3) – H(7)	0. 1093(6)	0. 1104(4)	0. 1093(13)	0. 1085(7)

* The values for the heavy-heavy bond lengths are corrected for thermal motion effects (using the TLS method).

Table 6 The structure data of bond distances (nm)and angles (°)

Structure	T/K	Charge	Acceptor	C _α – H(2)	H(2)···O(1)	C _α ···O(1)	C _α – H(2)···O(1)
L-alanine	295	Zwitterionic	CO ₂ ⁻	0. 1090(5)	0. 2438	0. 3474	158. 3
	60	Zwitterionic	CO ₂ ⁻	0. 1097(3)	0. 2391	0. 3445	160. 6
D-alanine	295	Zwitterionic	CO ₂ ⁻	0. 1098(8)	0. 2415	0. 3467	160. 1
	60	Zwitterionic	CO ₂ ⁻	0. 1099(4)	0. 2378	0. 3436	161. 0

Both the dihedral angles and the torsion angles in the gas phase and solution are difficult to evaluate, so the studies of Quack^[21] and Kitayama^[24] consider only the conformational factors in theoretical significance. Due to the lack of accurate experimental gas-phase structures for alanine conformers and the solvent effects in solution, we select crystal state to search for the E_{PV} . Based on the neutron diffraction data, we confirm that L-alanine is more stable than D-alanine

3.5 Contribution of C_α – H···O hydrogen bond interaction

The existence of C_α – H···O hydrogen bond in alanine has been proposed^[25]. The structural properties of C_α – H···O interactions generally parallel to those of the stronger O – H···O and N – H···O hydrogen bonds. Thomas Steiner^[26] systematically studied the weak hydrogen bonding of C – H···O interactions in 16 high-precision neutron crystal-structure determinations of α -amino acids. Neutron diffraction data of amino acid C_α – H suggest the lengthening of the covalent C_α – H bond in C_α – H···O interactions. We examined the interactions of D- and L-alanine crystal structure on a H···O distance ranging from 0. 2378 nm to 0. 2438 nm and C_α – H···O angle ranging from 158. 3° to 161. 1°. The calculated geometric parameters associated with the C_α – H···O interactions are presented in Table 5, 6. Using the criterion H···O < 0. 27 nm, C – H···O > 90°^[27], the existence of hydrogen bonds in alanine is confirmed.

Since the Salam phase transition is reversible, the bond lengths C_α(2) – H_α(2) of D-alanine(0. 1099 nm) at 295 K and

60 K are almost the same. It is coincident with the observation of Raman spectra of D-alanine, the second order C_α – H deformation modes vanished at 270 K but reappeared at 100 K. The results provide the evidence of symmetric breaking at $T_c \approx 250$ K and symmetry restoration at low temperature 60 K. We consider to determine the neutron structure of D-alanine at 270, 260, 250 and 240 K further.

4 Conclusion

Temperature-dependent neutron diffraction data show the crystal lattice distortion and the NH₃⁺ torsional motion in alanine enantiomers. Combining the theoretical calculation and the experimental results, L- alanine is more stable than D-alanine in crystal state. The low temperature structures (60 K) of the two enantiomers are likely to be similar, which implicates the predicted phase transition D $\rightleftharpoons$ L being reversible. Salam proposed an amplification mechanism based on quantum mechanical tunneling. The chirality can be amplified, once it appears. The molecules are easily transferred to polymers on their surface. Giant chiral molecules such as polymers, and especially crystal lattices, may have much larger E_{PV} ^[28].

In conclusion, we argue that the weak force is the only universal chiral influence. The world is made of fermions, which interact by exchange bosons. The electrostatic repulsion between two electrons is mediated by exchange of virtual phonons. Pre-biotic symmetry breaking is a pre-condition for life. The indirect universal systematic influence of the electroweak interactions on

the prebiotic-biotic transition, through the parity-violating energy differences in enantiomer crystals, may have specifically the contribution to the terrestrial biomolecular homochirality.

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手性分子中的宇称破缺: D- 和 L- 丙氨酸的变温中子结构研究*

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摘要 利用单晶的中子衍射研究 295 K 和 60 K 时丙氨酸对映体的结构特征以及由 D 到 L 构型转变的可能性. 中子衍射数据揭示了变温过程中产生的晶格扭曲和 NH_3^+ 的扭转. 通过分析宇称破缺能差 E_{PV} 随二面角及扭角的变化, 肯定了 D- 丙氨酸能量高于 L- 丙氨酸的结论. 降温过程中 D- 和 L- 丙氨酸的弱氢键的行为的差异表明, 可能是由于电弱相互作用宇称不守恒所引起. 丙氨酸中子结构再次证实 $\text{C}_\alpha - \text{H} \cdots \text{O}$ 氢键的存在. 然而, 比较 295 K 和 60 K (高于和低于丙氨酸相变温度 250 K) 的中子衍射结构数据, 表明并没有发生 D 型到 L 型的构型转化, 这意味着 Salam 相变不是传统意义的结构相变.

关键词: 宇称破缺, 分子手性, 中子衍射, D- 和 L- 丙氨酸

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