Temperature-dependent magnetic susceptibilities study on parity-violating phase transition of D- and L-alanine crystals

Wenqing Wang,[a,*] Wei Min,[a] Fan Bai,[b] Lin Sun,[a] Fang Yi,[a] Zheming Wang,[c] Chunhua Yan,[c]
Yongming Ni[d] and Zhongxian Zhao[d]

[a]*Department of Applied Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China*
[b]*Department of Physics, Peking University, Beijing 100871, China*
[c]*State Key Laboratory of Rare Earth Materials Chemistry and Applications, Peking University, Beijing 100871, China*
[d]*National Laboratory for Superconductivity, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*

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Abstract—Temperature-dependent DC-magnetic susceptibility measurements were employed to test the parity violating effect in a specific phase transition of alanine crystals. An obvious difference in magnetic susceptibility between the two enantiomers was observed at temperatures lower than the transition point $T_c \approx 250$ K. A vibrationally generated electronic ring current model was introduced to explain this phenomenon. This parity-violating phase transition of D-alanine may be closely related to the one suggested by Salam. The different behavior of the D- and L-amino acids below the transition temperature may result in new insights into the application of low temperature e*nantiomeric separations* and the origin of homochirality. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Our universe, and hence our visible world, is inherently chiral. The homochirality of biological molecules has long been known to be an important characteristic of life. Since it was suggested in the early 1970s that an electroweak interaction would lift the degeneracy between enantiomers,[1,2] it has been widely discussed whether the parity-violating weak neutral current (WNC) at the molecular level can be a potential candidate for the homochiral scenario under terrestrial and extraterrestrial conditions.[3–7] While the phenomenon of the parity violation (P-odd) effect in atoms is now well established,[8] few experiments exist today with positive results showing P-odd effects in molecular physics, because WNC induces hardly any observable effects between enantiomers in their ground states owing to the tiny parity-violating energy difference (PVED $\approx$ 10^{-18} eV) and negligibly small (10^{-15}%) enantiomeric excess in racemates.[9–11] Therefore, PVED has become important not only to explain the selection of the L-amino acids in the origin of life, but also as a 'molecular footprint' of fundamental physics.[12]

Theorists also proposed several possible amplification and effective detection mechanisms for the P-odd effect, including polymerization and crystallization, molecules containing heavy isotopes, double-well potential systems and phase transition systems.[13–15] In 1991 Salam[14,15] proposed that the subtle energy difference of chiral amino acid molecules induced by Z^0 interactions in combination with Bose condensation produced proteins as a consequence of a second-order phase transition below a critical temperature T_c. The idea is supposed to start from the Feynman Lagrangian methodology of the BCS theory for the superconducting electronic system. By using Sakata's formula, the following result is reached.

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

Here, the φ field is expressed as a complex auxiliary Higgs scalar field, g_{eff} is an attractive coupling constant between electrons of opposite spin states, θ is the Weinberg angle. Salam took $(1-4\sin^2\theta) \approx 1/13$, $\sigma(0) = m_z^2$ with the empirical value of the parameter $\sin^2\theta \approx 0.231$, and got $g_{eff}\,\sigma(0) \approx 1$.

Because of its relatively simple structure, alanine has been used as a prototype to test the Salam phase transition hypothesis. We have first confirmed a parity-violating phase transition around 260 K of D-alanine

* Corresponding author. E-mail: wangwq@sun.ihep.ac.cn

and valine crystals by specific heat measurements with differential scanning calorimeter.[16] It has been suggested that the measurement of DC-magnetic suscepti-bilities is an efficient and sensitive tool for detecting molecular magnetic behavior during phase transition process. In the work described herein, temperature-dependent DC-magnetic susceptibility measurements were employed to test the P-odd effects in the afore-mentioned parity-violating phase transition of alanine enantiomers.

2. Experimental

2.1. Sample preparation and characterization

D- and L-Alanine were obtained from Sigma Chemical Corporation. The single crystals, which were grown by slow evaporation of saturated aqueous solutions at 4°C, then washed with absolute alcohol, placed under vac-uum and kept in a desiccator, were well-formed and elongated along the c axis.

The purity of the D- and L-alanine single crystals were characterized by elemental analysis (C, H and N), and a good agreement was shown between theoretical and experimental data. By using X-ray diffraction crystal-lography on a Rigaku RAXIS-RAPID imaging plate diffractometer at 300 K, the crystal structure of D- and L-alanine have been determined and refined by analysis of complete three-dimensional diffraction data from Mo-K_α X-radiation. The crystals of D- and L-alanine are orthorhombic with the same space group $P2_12_12_1$, $Z=4$, with lattice constants $a=6.0344$, $b=12.3668$, $c=5.7879$ Å, $\alpha=\beta=\gamma=90°$, $V=431.93$ Å^3, which agrees with Simpson's data.[17] This indicated that D- and L-ala-nine are pure single crystals containing no water of crystallization.

2.2. DC-magnetic susceptibilities measurements

The magnetic moment (m) and magnetic susceptibility (χ_ρ) of D-/L-alanine crystals were measured using a SQUID magnetometer (Quantum Design, MPMS-5) from 200 to 300 K at a field of 1.0 and −1.0 T. Because the magnetization variation per sample was close to the baseline resolution of the magnetometer, the sample crystal was held directly in the center of a plastic straw purely by friction without using a sample holder. Crys-tals were weighed and transferred to the straw. The signal from the plastic straw was cancelled out while the temperature was measured.

Magnetization measurements (shown in Figs. 1 and 2) have shown alanine enantiomers to be diamagnetic, since they have even numbers of electrons which form closed, magnetically neutral shells. It is clearly indicated that both values and variations of magnetic susceptibil-ities of D- and L-alanine enantiomers remain the same when the temperature is above 250 K, and there is no distinct difference between them. In contrast, when the temperature is lowered to <250 K, D-alanine undergoes a magnetic phase transition and the χ_ρ values experi-

ence a peak near 250 K, while the χ_ρ values for L-alanine vary slowly and continuously. The experimen-tal results are reproducible over several thermal circles from 200 K through to 300 K, which indicates that this behavior is completely reversible for D- and L-alanine crystals. For different pairs of D-/L-samples, we observed the same temperature-dependent χ_ρ behavior characterized by approximately the same transition temperature.

Interestingly, while the temperature varies in the range of 200~250 K, χ_ρ values of D-/L-alanine are nearly opposite the χ_ρ value of D-/L-alanine at 250 K taken as the base value 0. This may give some clues for the WNC playing a contrary maybe parity-violating role in the magnetic behavior of D- and L-alanine molecules in this temperature range.
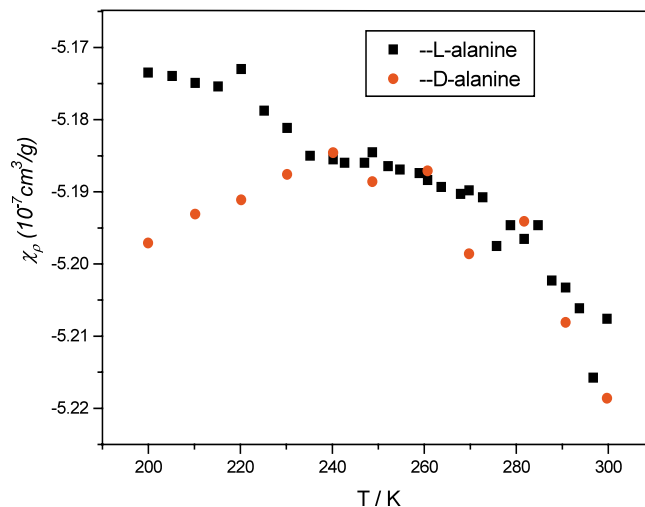
Figure 1. Temperature dependence of magnetic susceptiblity at a field of 1.0 T.
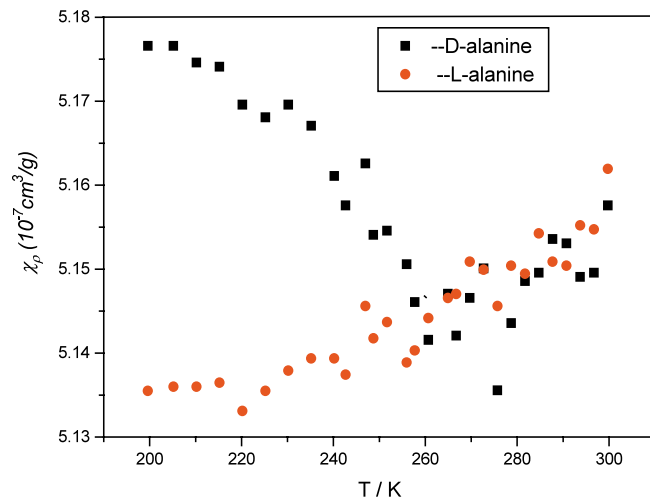
Figure 2. Temperature dependence of magnetic susceptiblity at a field of −1.0 T.

3. Results and discussion

3.1. Evidence of second-order phase transition by differential specific heat analysis

The temperature dependence of the specific heats of D-/L-alanine and valine crystals have been measured by differential scanning calorimetry with adiabatic continuous heating in the temperature region from 77 K through to 300 K.[16] It was found that an obvious λ phase transition around 260 K existed in D-alanine and D-valine crystals but not in the L samples. The experimental results were repeated for the same samples after several thermal cycles from 77→300 K. The shape and magnitude of the specific heat jump and the peak position are approximately the same for different pairs of D-/L-samples, which shows that the phase transition is reproducible and reversible.

### 3.2. Magnetic susceptibilities as a probe of molecular chirality

In order to understand the microscopic particulars about molecular chirality hidden behind the anomalous magnetic susceptibilities behavior, a vibrationally generated electronic ring currents model (shown in Fig. 3) proposed by Freedman at al.[18] was introduced to explain the parity-violating phenomenon shown in our magnetic susceptibilities measurements. In the case of alanine crystal, the C_α–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, m. As depicted in Fig. 3 for the C_α–H contraction (or lengthening) in D-alanine, positive (or negative) current flowing in the direction N→C_α when electrons are injected into the ring by the C_α–H contraction (or lengthening), produces a magnetic dipole transition moment, m, with a component in the direction of the electric dipole transition moment μ. The rotational strength $R = Im (\mu \cdot m)$, is positive (or negative), as observed experimentally. The main difference between enantiomers lies in the fact that they produce opposite optical rotation due to

the opposite sign of Im $(\mu \cdot m)$. We will next discuss the origin of the difference of m between D- and L-crystals.

3.3. Discussion of the phase transition mechanism

3.3.1. Temperature-dependent Raman spectra study. Vibrational spectra of D- and L-alanine single crystals were measured using a Ranishow 1000 Micro-Raman system from 200 K through to 300 K. The laser beams with different polarization have different selection rules for Raman spectra of alanine crystals. A further observation of this phase transition in D-alanine by Raman spectra showed that when the temperature exceeds the transition temperature $T_c \approx 250$ K, the spectra of C_α–H modes at 1305 cm^{-1} (C_α–H bending), 2964 cm^{-1} (C_α–H stretching) of D-alanine show an obvious variation in its peak positions (Figs. 4 and 5). As the temperature exceeds T_c, 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 at about 250 K. However, as for the C_α–H bending and stretching modes of L-alanine, our Raman spectra study did not indicate any frequency changes from 200 K through to 300 K. A previous temperature-dependent Raman study about L-alanine single crystal conducted by Storms et al.[19] did not display any frequency variations of C_α–H bending and stretching modes either. Since the vibrational frequencies of C_α–H bending and stretching modes are very sensitive to the change of electric dipole moment μ in the vibrationally generated electronic ring current model, the sudden frequency shift of 1305 and 2964 cm^{-1} modes of D-alanine suggests the sudden variation in the electric dipole moment μ in D-alanine when the temperature is below 250 K. This phenomenon is of great importance for the understanding of measurement results from temperature-dependent magnetic susceptibilities.

3.3.2. Different dihedral angle of D- and L-alanine at transition temperature. Berger and Quack[20] conducted a detailed analysis of dynamic chirality, which proved that the dihedral angle between the O_2C and C_α–H planes (Fig. 6) plays an important role in determining the intrinsic energies of the alanine molecules. This difference has been used in the calculation of PVED. In this study, the unit cell dimensions and cell parameter of X-ray crystallographic data were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite monochromated Mo-K$_\alpha$ radiation at 270 and 250 K, respectively, and dihedral angles between the O_2C and C_α–H planes were calculated from the atomic coordinates of O(1) O(2) C(1) C(2) H(1) of D- and L-alanine (Table 1).[21] The most striking and important result of this part of the study is the apparent difference in the dihedral angle between D- and L-alanine at 250 K. In the electronic ring current model described in Section 3.2, the obvious dihedral angle change of D-crystal (45.52(30)↔43.97(28)°) must surely be accompanied by an alteration in the relative atom positions and the electron distribution in the five-membered ring, which will inevitably make the producing process (μ→m) of the magnetic dipole transition moment vary significantly.
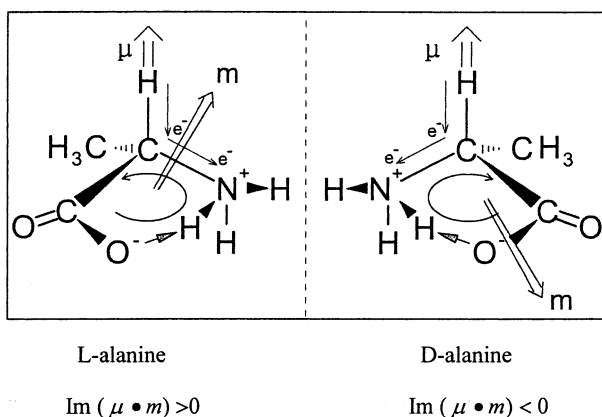
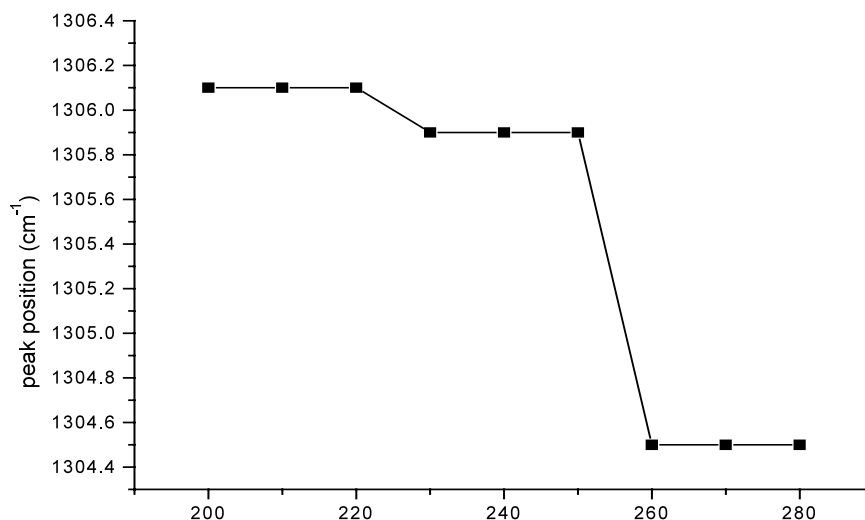**Figure 3.** Vibrationally generated ring currents in alanine enantiomers.

Figure 4. Peak position of 1305 cm^{-1} of Raman spectra ($\parallel$, $\parallel$) versus T for D-alanine.
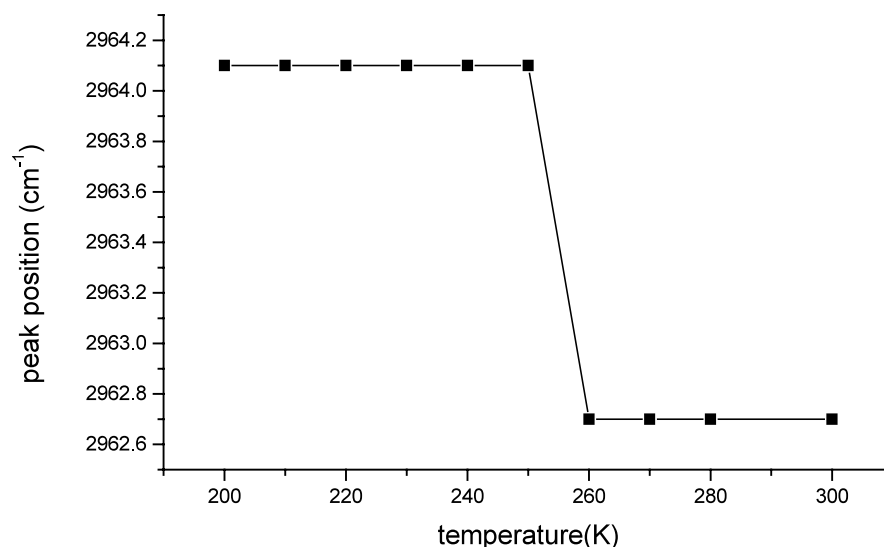

Figure 5. Peak position of 2964 cm^{-1} of Raman spectra ($\parallel$, $\parallel$) versus T for D-alanine.

3.3.3. Microscopic details of the parity-violating phase transition. From the above model, we can make a sound explanation of the observed phenomena. The Raman spectra have confirmed that the phase transition is accompanied by a change in the electric dipole moment μ for D-alanine. In addition, the change of dihedral angle of D-alanine will ultimately result in the apparent variation of the producing process ($\mu \rightarrow m$) of the magnetic dipole transition moment. Since μ and $\mu \rightarrow m$ of D-alanine all undergo a sudden change in their magnitudes when the temperature exceeds T_c, it is reasonable to observe the anomalous variation of m for D-alanine in this phase transition because it is closely related to μ and $\mu \rightarrow m$.

4. Summary

The parity-violating low-temperature magnetic suscepti-bility behavior of D- and L-alanine crystals, together with the λ phase transition measured by differential scanning calorimetry, provides a significant insight into the role played by weak neutral current in the low-tem-perature phase transition and physical properties of
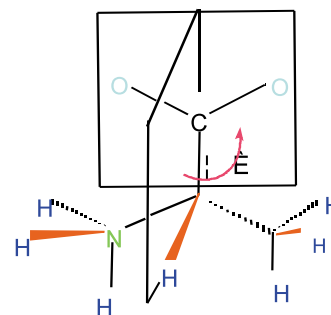

Figure 6. Conformation of the zwitterionic form of L-alanine with explicit definition of the angle θ between the O$_2$C and C$_\alpha$–H$_\alpha$ planes.

Table 1. X-Ray diffraction data for D-, L- alanine single crystals at 270 and 250 K

Temperature				270 K			
Samples		D-Alanine				L-Alanine	
Empirical formula				$C_3H_7NO_2$			
Formula weight				89.10			
Crystal system				Orthorhombic			
Space group				$P2_12_12_1$			
Unit cell		$a = 0.60073(5)$				0.60095(5)	
		$b = 1.23030(7)$				1.23388(7)	
		$c = 0.57732(4)$				0.57904(3)	
Volume (nm^3)		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(1)	0.441(2)	0.237(1)	0.656(2)	0.440(2)	0.238(1)	0.656(2)
Dihedral angle	θ	**45.52(30)°**				**45.20(29)°**	
Temperature				250 K			
Samples		D-Alanine				L-Alanine	
Empirical formula				$C_3H_7NO_2$			
Formula weight				89.10			
Crystal system				Orthorhombic			
Space group				$P2_12_12_1$			
Unit cell		$a = 0.06004(3)$				0.60002(4)	
		$b = 1.2379(5)$				1.2393(6)	
		$c = 0.57892(3)$				0.57822(2)	
		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(1)	0.437(2)	0.237(1)	0.653(2)	0.440(2)	0.237(1)	0.658(2)
Dihedral angle	θ	**43.97(28)°**				**45.72(30)°**	

amino acids. As for the transition temperature and its characteristic of parity violation, this parity-violating phase transition of D-alanine may be closely related to the one suggested by Salam. However, this cannot be simply interpreted as the configuration change of D→L because of the evident divergence of D- and L-enantiomers in the low-temperature physical properties of magnetic susceptibility, vibrational frequencies of C_α–H bending and stretching modes, and the dihedral angle between the O_2C and C_α–H planes. Had the D-sample transferred to L-, the low-temperature physical properties of them would have been the same. In addition, the fact that D- and L-alanine experience different behavior below T_c may be very important in the application of enantiomeric separations at low temperatures.

Acknowledgements

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