Journal of Biological Physics **22:** 65–71, 1996.

Susceptibility Behaviour and Specific Heat Anomaly in Single Crystals of Alanine and Valine

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(Received 12 February 1996; accepted 23 February 1996)

Abstract. Magnetization of single crystals of D-, L-alanine and D-valine were measured as a function of temperature using the SQUID magnetometer. An obvious lambda transition at 270 ± 1 K was shown in the specific heat measurement of alanine and valine enantiomers by differential scanning calorimetry (DSC). Magnetic transition temperature seems coincident with that of lambda transition. Temperature dependence of the X-ray powder diffraction for D-valine showed no crystal lattice change under the temperature cooling down from 293 K to 123 K. We propose that the difference of the $\chi \sim T$ curve between the D-alanine and L-alanine is attributable to the variation of intramolecular geometry of chirality density in the presence of an external magnetic field. The chirality characteristics of alanine and valine enantiomers by the specific heat and susceptibility behaviour are discussed.

Key words: Alanine and valine enantiomers, Chirality, Magnetic transition, Specific heat anomaly

1. Introduction

Why do all the amino acids from which proteins are formed twist to the left in all known organisms? That's the crux of a scientific mystery [1]. Scientists have hunted for physical forces on Earth or from an extraterrestrial source. Recently, Salam suggested that chirality among the twenty amino acids which make proteins may be a consequence of a phase transition [2, 3]. According to Salam's hypothesis, at the end of chemical evolution a particular cooperative phenomenon, namely, a phase transition beneath a certain critical temperature T_c took place. Amino acids that had been synthesized earlier from various precursors entered into a new phase, which was a Bose condensed mode, analogous to that of BCS superconductivity [4].

An experimental probe of the existence of a proposed phase transition is to lower temperature while measuring the differences of specific heats and observe the anomalies in the curve of C_p vs T. In the case of superconductivity, one of the characteristic features associated with a phase transition of the Bose condensation type is a marked discontinuity in the magnetic susceptibility which occurs in addition to the specific heat effects accompanying the transition. Therefore we decided to apply an external magnetic field to measure the magnetic moment and corresponding mass susceptibility and look for the magnetic phase transition to determine T_c.

Thus, the purpose of the present work is to: (1) establish a phase transition by further measuring the specific heat for a particular amino acid from 100 to 300 K; (2) elucidate the property of such a phase transition by examining the mass susceptibility of the same sample.

2. Experimental Tests for the Proposed Phase Transition in Alanine and Valine

Alanine and valine enantiomers were selected since alanine molecules could withstand temperatures as high as 700 K for 1 sec and remain stable and intact upon impact with the Earth [5]. The parity-violating weak interactions give rise to L and D configurations of alanine and valine with energy differences of -3.0 and -6.2×10^{-19} eV respectively [6].

2.1. SPECIFIC HEAT MEASUREMENTS

Valine and alanine enantiomers were obtained from the Sigma Chemical Co. and were crystallized by slow evaporation of saturated aqueous solution, then washed with absolute alcohol, evacuated and kept in a desiccator. C, H, N element analysis showed that the samples did not contain any crystal water and was in high purity [7]. Additionally, the water content in all samples before and after cooling was detected to be less than 10 ng by Infra Photoacoustic Spectra.

The differential specific heats for D-, L-alanine and D-, L-, D, L-valine single crystals were determined by an adiabatic continuous heating method [8]. The experiments were performed on D-alanine 113.30 mg, L-alanine 99.40 mg, D-valine 67.47 mg, L-valine 22.65 mg and D, L-valine 37.6 mg have been carried out. The differential specific heat was measured with increasing temperature from 77 to 300 K. The temperature scanning speed was set to 0.5 K/min in the region and the accuracy was better than ±1 K at the measured temperature range.

2.2. DC MAGNETIZATION MEASUREMENTS

Magnetic moment (m) and magnetic susceptibility (χ_ρ) of D-, L-alanine and D-valine single crystals were measured by a SQUID magnetometer (Quantum Design, MPMS-5) at a field of 1 kG (with differential sensitivity 1E-8 EMU to 1 Tesla) in the temperature range from 5 K to 290 K. Because the magnetization change per sample was close to the baseline resolution of the magnetometer, care was needed to design the sample holder. A straight piece of plastic straw was used with a length of 6 cm and i.d. of 3 mm. Since the i.d. of the plastic straw was close to the diameter

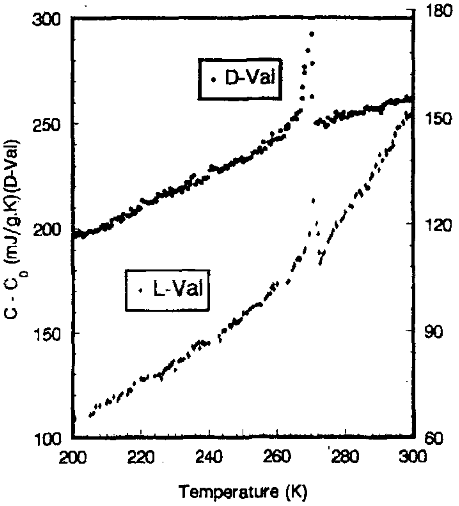

Figure 1. Temperature dependence of the specific heat of D-valine and L-valine single crystals.

of the sample crystal, the sample was held directly in the center of the straw purely by friction without a sample holder. Crystals were weighted and determined to be 174.1 mg (D-Ala), 99.5 mg (L-Ala) and 148.8 mg (D-Val), then transferred to the straw. The signal from the plastic straw was canceled out while the temperature was measured. In experiments, we used large crystals which were grown employing a crystal fragment technique.

3. Results and Discussion

In our specific heat measurements (Figure 1 and Figure 2), it was found that valine and alanine enantiomers all showed an obvious phase transition at 270 ± 1 K by differential scanning calorimetry with an adiabatic continuous heating method [7, 8]. However, GC capillary enantiomeric column analysis has shown no enantiomer variation before and after the cooling DSC measurement [8]. The X ray powder diffraction analysis made on a Rigaku D/MAX-A using monochromat high intensity Cu-K showed that no crystal lattice change in D-valine under temperature cooling down from 293 K, 273 K, 263 K and 123 K [9]. Although Grunenberg A. *et al.* [10] studied 22 crystalline aliphatic amino acids including L- and D, L-valine by DSC in the temperature range 233 to 423 K, the phase transition for both valines has not been observed [10].

Figure 1 shows that the specific heat C_p value of D-valine is larger than that of L-valine and the same relationship existed in alanine enantiomers. Actually, the specific heat of crystal was influenced by the lattice and electronic structure. However, the result from X ray powder diffraction demonstrated that the effect of the crystal lattice on C_p could be excluded and the phase transition observed might be ascribed to the electronic structure. Magnetization measurements have shown

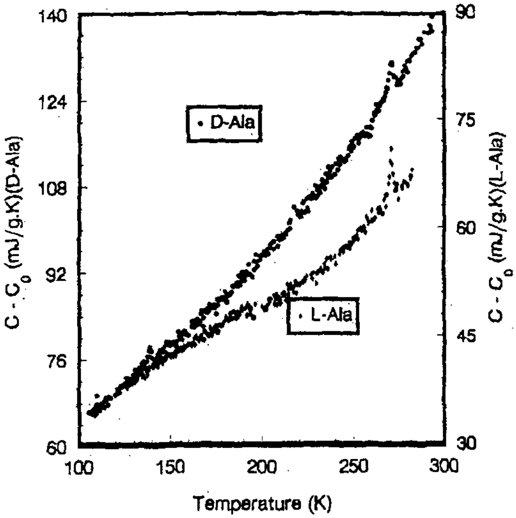

Figure 2. Temperature dependence of the specific heat of D-alanine and L-alanine single crystals.

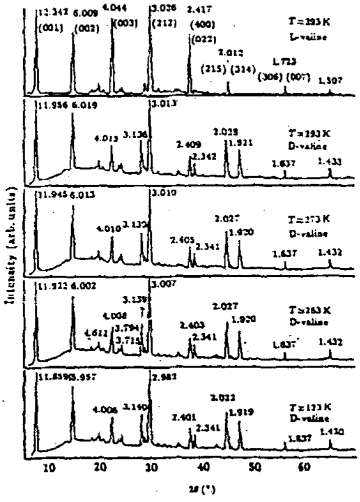

Figure 3. The X ray powder diffraction patterns of D-valine and the L-valine single crystal samples at different temperature. (Internal standard: Si (3.138, 1.92); Al(2.342)).

valine and alanine enantiomers to be dimagnetic, since they have even numbers of electrons which form closed, magnetically neutral shells. Such characteristics might be related to the differences in degrees of freedom between D- and L-amino acid molecules. It is in agreement with the hypothesis of Salam and the quantum mechanical calculation by Mason [6]. In all cases, the biologically dominant L-enantiomer was found to have lower energy and the specific heat value reflects this fact.

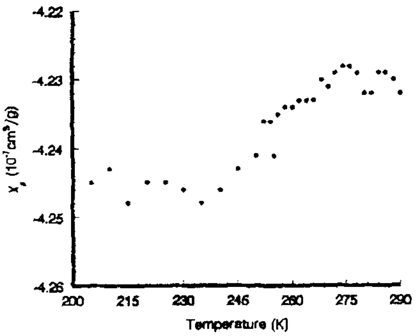

Figure 4. Mass susceptibility (χ_ρ) vs Γ for D-alanine at $H = 1$ kG for $T = 200$ K to 290 K.

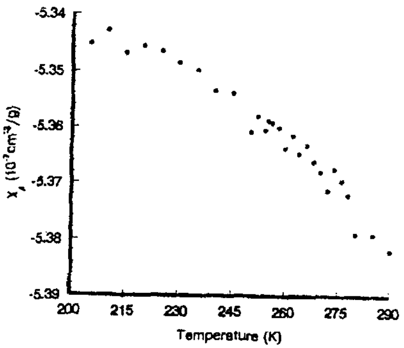

Figure 5. Mass susceptibility (χ_ρ) vs T for L-alanine at $H = 1$ kG for $T = 200$ K to 290 K.

Figures 4–6 show the magnetization measurements of D-, L-alanine and D-valine vs temperature (T) in a field of 1 kG. Weak diamagnetism were observed in all three cases. Their magnetic susceptibilities are negative $(\chi_\rho < 0)$, the values are very low and in absolute value about 10^{-7} cm^3/g. In Figures 4, 5 and 6, we present the temperature dependence of the susceptibilities of D-alanine, L-alanine and D-valine from 200 to 290 K and find that the temperature at which the discontinuity

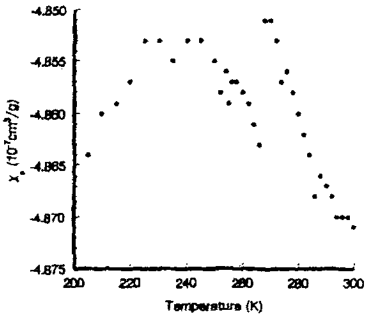

Figure 6. Mass susceptibility (χ_ρ) vs T for D-valine at $H = 1$ kG for $T = 200$ K to 300 K.

of magnetic susceptibility occurs for D-alanine and D-valine is coincident with T_c specific heat measurement. Figures 4 and 5 also show that the χ_ρ vs T is different for D- and L-alanine.

Based on the above result, it might be proposed that the difference of the $\chi \sim T$ curves for D-alanine and L-alanine can be attributed to the variation of intramolecular geometry of chirality density, which is related to the parity violating energy shift of a chiral molecule and is a consequence of the short range of the weak interaction between the nuclei and electrons. The discontinuity in magnetic susceptibility might be induced by the occurrence of polarization phenomena. Quantum mechanical theory indicates that the magnetic susceptibility of a system with weakly interacting particles, for the case where the electron clouds of the particle are not spherically symmetrical, will be composed of two parts: (1) precession diamagnetism, (2) Van Vleck polarization paramagnetism. At elevated temperature, the role of polarization paramagnetism will be greater (in the D-case), while in the L-case, the orientation paramagnetism which decreases with temperature predominantly affects the magnetism [12]. Thus, different magnetic behaviour for D-, L-amino acids has been observed in our experiments. Such observations as these, namely, the magnetic susceptibility of molecules in single crystal amino acids are the first to be reported [13].

Acknowledgments

This research was supported by Grants of the State Science Commission and the Doctoral Program Foundation of the Institution of Higher Education and we thank professor Dai Daosheng for helpful discussions.

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