



THERMAL CONDUCTIVITY OF SINGLE CRYSTAL L-ALANINE

R.S. Kwok^{a,b}, P. Maxton^{a,b} and A. Migliori^a

^a Physics Division, Los Alamos National Laboratory, Los Alamos, NM 87545

^b Physics Dept. and Solid State Science Center, Univ. of California, Los Angeles, CA 90024

(Revised manuscript received 2 April, 1990 by A.A. Maradudin)

The speed of sound and thermal conductivity of L-alanine single crystals have been measured. The longitudinal speed of sound was measured by a pulse echo technique and the thermal conductivity by a steady-state linear heat-flow method. The long mean free path at low temperatures indicate that the specimen under study is relatively clean. The thermal conductivity drops exponentially to a minimum at room temperature without displaying any $1/T$ dependence suggesting that the lattice modes are strongly anharmonic.

As one of the simplest amino acids, L-alanine has attracted much interest in the study of protein dynamics. In addition, single crystal L-alanine has shown strongly non-linear behavior and anomalous phonon coupling^{1,2}, and has been suggested as a system exhibiting vibrational solitons². Such solitons might arise as a result of non-linear coupling between an optical lattice mode and the acoustic phonons. To study one aspect of the phonon non-linearity and to characterize the heat transport in this material, we have measured the longitudinal speed of sound and thermal conductivity along the c-axis of L-alanine crystals.

L-alanine ($\text{CH}_3\text{-CH-NH}_2\text{-CO}_2$) forms clear, colorless, orthorhombic crystals. Our single crystals are grown by slow evaporation of saturated solutions of commercially available reagent grade L-alanine dissolved in distilled, deionized water. Typical growth time is two to three weeks. The largest crystals are approximately $25 \times 12 \times 9 \text{ mm}^3$. The sample used for thermal conductivity measurement has a dimension of $20 \times 2.1 \times 1.5 \text{ mm}^3$, with the longest side parallel to the c-axis.

The longitudinal speed of sound was measured on a variety of samples using a pulse echo technique. Samples were machined on an air bearing lathe to produce optically smooth, parallel faces. These faces were perpendicular to the c-axis and nominally 0.25 inches apart. A single transducer of Y-cut lithium niobate was attached to one of these faces using vacuum grease as an acoustic coupling fluid. The transducer was driven with pulses of 30, 90 and 150 MHz RF from a Matec model 7700 transceiver. Typically, we observed more than 10 echoes, with the best measurements yielding as many as 50. We measured a longitudinal speed of sound of 6.2 km/s at room temperature.

Neutron scattering studies³ also show that the longitudinal speed of sound along the c and a-axes are 6 and 4 km/s respectively. The transverse speed of sound are almost identical and have a value of $\approx 2 \text{ km/s}$. Although the speed of sound of the 3 acoustic branches along the b-axis have not been measured, they are expected to be similar to that of the a-axis.

At low temperatures where the Debye model is valid, one can estimate an isotropic averaged speed of sound by :

$$\bar{v} = \frac{\int \sum_j v_j g_j(\omega) N(\omega) d\omega}{\int \sum_j g_j(\omega) N(\omega) d\omega}, \quad (1)$$

where v_j is the speed of sound for the j th acoustic branch, $g_j(\omega)$ is the density of states which is inversely proportional to v_j and $N(\omega)$ is the occupation number of the phonon mode with energy $\hbar\omega$. From the neutron scattering results, we calculated an average speed of sound to be 2.5 km/s which is in good agreement with the 2.6 km/s deduced from low temperature specific heat data⁴. Incidentally, using Eq.(1) and the neutron scattering data, the average speed of sound (v_c) along the c-axis is also calculated to be 2.6 km/s. Analyses on thermal transport along the c-axis are based on this value of v_c . Following Daurel et al.⁴, we treat L-alanine as a molecular solid with 6 degrees of freedom per molecule and obtain a Debye temperature θ_D of 205 K.

The thermal conductivity κ was measured by a steady-state linear heat-flow method. Radiative heat losses were minimized using a stainless steel heat shield with a diameter about three times the sample width. The shield temperature was controlled at one end and anchored to a thermal reservoir at the other so that the temperature profile of the shield matched to that of the sample. The apparatus has been calibrated, from 4 to 300 K, with a fused quartz rod as well as a stainless steel rod of similar dimensions; results agreed well with the literature. Absolute errors are estimated to be $< 10\%$ from geometrical effects. Our relative precision was better than 0.5% mostly from instrumental errors. The details of the apparatus have been reported elsewhere⁵. Data in this work were taken between 7 K and 292 K.

Figure 1 shows a plot of the observed thermal conductivity vs temperature. At low temperatures, the measured κ is typically that of an insulating crystal;

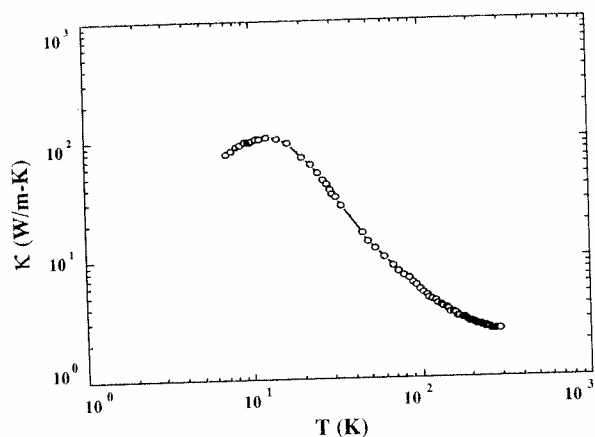


Fig.1 Thermal conductivity of l-alanine from 7K to room temperature in log-log scale.

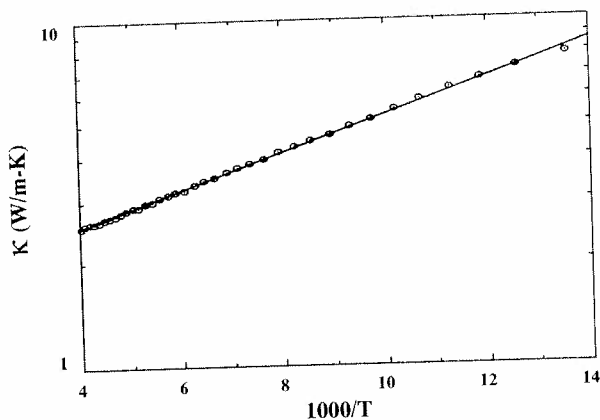


Fig.2 $\text{Log}(\kappa)$ vs $1/T$ of the same data shown in Fig.1 for $70\text{K} < T < 250\text{K}$. The straight solid line displayed in figure shows that κ decreases exponentially as temperature increases in this regime.

with a maximum due to the decrease of Umklapp processes and the surface/impurity effect⁶. The most striking feature of this plot is the absence of power law behavior at high temperatures. From a Peierls prediction for an insulating single crystal, one expects :

$$\kappa \propto T^3; \text{ for } T \ll \theta_D \quad (2a)$$

$$\kappa \propto \exp[\theta_D/\alpha T]; \text{ for } T < \theta_D \quad (2b)$$

$$\kappa \propto 1/T; \text{ for } T \geq \theta_D \quad (2c)$$

$$\kappa \propto \kappa_{\min}; \text{ for } T \gg \theta_D \quad (2d)$$

where α is a numerical constant in order of unity. Most molecular crystals follow this prediction⁷. In l-alanine, contrary to this picture, the power law behavior is absent for $T \approx \theta_D$. We observed instead, an exponential temperature dependence from approximately 70 to 270 K with a smooth transition to a nearly temperature independent minimum thermal conductivity of about 2.5 W/m-K. Figure 2 shows that κ follows Eq.(2b), for $70 < T < 250$ K, with an activation energy for Umklapp processes of 130 K which corresponds to a Debye temperature of 205 K and $\alpha=1.6$.

If the room temperature value of the thermal conductivity is indeed approaching its minimum, the mean free path calculated from Fig.1 should be approaching a value in order of a lattice constant. Plotted in Fig.3 is the phonon mean free path λ calculated from :

$$\lambda = 3\kappa/Cv_c, \quad (3)$$

where C is the specific heat per unit volume of the excitations responsible for heat transport. Note that at 7 K, we estimate a value of 20 μm for λ . This relatively long mean free path testifies to the purity of the sample.

To obtain a value for λ at higher temperatures requires a more detailed consideration of the specific heat. If we assume that all the heat is carried by acoustic phonons, the appropriate expression for C can be calculated⁴ by fitting a Debye model to the low temperature specific heat. Following this model, we estimate a λ in excess of 50 Angstroms at high temperatures. Since the lattice constant along the c -axis is only 5.784 Angstroms⁸, we conclude that

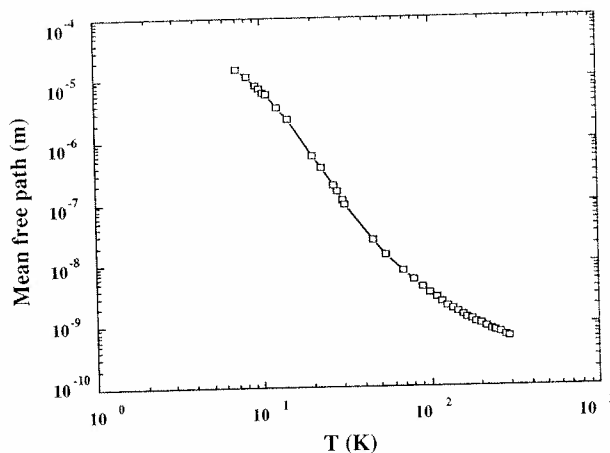


Fig.3 Phonon mean free path as calculated from Eq.(3). Solid line is a guide to the eye.

acoustic phonons are not the only excitations involved in heat transport. We propose instead that, at high temperatures, a significant amount of heat is also carried by the low lying optical modes. L-alanine has 4 molecules per unit cell which give rise to 21 lattice modes. These modes, together with the anisotropic acoustic branches, account for most of the heat capacity. If we insert the total specific heat into Eq.(3), the room temperature mean free path drops to approximately 6 Angstroms, which is believable as a minimum. However, this estimation assumes that both the optical and acoustic branch excitations travel at the acoustic branch speed of sound and is therefore an underestimate.

We follow Slack⁹ in estimating the optical phonon contribution to the minimum thermal conductivity:

$$\kappa_{\min}^{\text{optical}} \approx \frac{1}{3} \frac{k_B a}{\sigma} \left(\sum \Omega^{(i)} \right) \delta, \quad (4)$$

where k_B is Boltzmann's constant, σ is the unit cell volume, $\Omega^{(i)}$ is the frequency of the i th optical mode, a is the unit cell dimension, and δ is the minimum mean free path. Because we are dealing with lattice modes, we have modified Slack's estimation for the high temperature speed of sound to (assuming that energy of each mode diffuses across the entire unit cell in one oscillation period):

$$v^{(i)} = a \Omega^{(i)}, \quad (5)$$

in obtaining Eq.(4).

We use Raman spectra to estimate the sum of frequencies in Eq.(4). Figure 4 shows the lattice-mode frequencies of l-alanine. Only 14 of the allowed 21 modes are discernible; each of the remaining 7 are presumed to be degenerate with one of the resolved modes. For purposes of estimating the minimum thermal conductivity, we sum the frequencies in Fig.4 and multiply by 3/2. We also take $\delta \approx 5.8$ Angstroms and obtain a value of 0.3 W/m-K for the optical phonon contribution to the thermal conductivity.

We also follow Slack in estimating the minimum thermal conductivity contributed from the acoustic modes - normally the dominant modes to heat transport in insulators:

$$\kappa_{\min}^{\text{acoustic}} \approx \frac{3}{2} \frac{k_B v_c^2}{\sigma \Omega_A}, \quad (6)$$

where Ω_A is the low temperature Debye frequency ($\hbar \Omega_A = k_B \theta_D$). This formula yields a value of 0.1 W/mK.

Thus, we observe what appears to be a minimum thermal conductivity of approximately 2.5 W/m-K and can account theoretically from the above analysis for only about 0.4 W/m-K. The source of this discrepancy is not obvious. An upper bound on the radiative contribution along the c-axis of only 0.6 W/m-K can be estimated by assuming ballistic transport for photons (an assumption that should not be valid across much of the room temperature black-body spectrum given the many IR absorption bands in l-alanine). Few intramolecular modes are populated at these temperatures and the sound velocities associated with these modes should be negligibly small. This factor of six

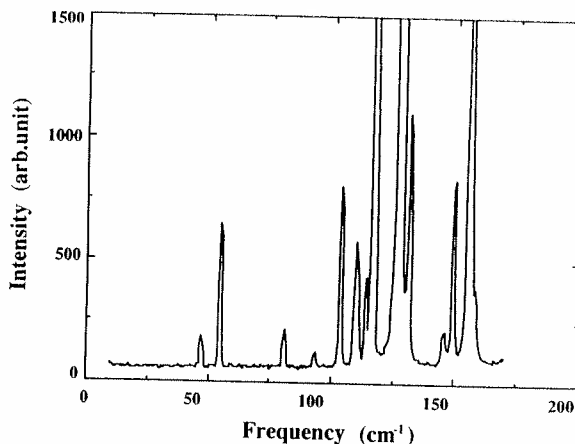


Fig.4 Lattice-mode frequencies of l-alanine measured at 50K.

discrepancy could be reconciled if a minimum mean free path of approximately six lattice constants could be justified.

In conclusion, we have measured the thermal conductivity of a single crystal l-alanine. The long mean free path at low temperatures indicates that the sample under study is relatively pure and defect free. A logarithmic decline in κ over a broad temperature range suggested an activation temperature for Umklapp processes of 130 K. The fact that the thermal conductivity steeply drops to a minimum before displaying $1/T$ dependence demonstrates significant lattice anharmonicities in the system. The observed high-temperature κ_{\min} of 2.5 W/m-K is larger, by a factor of six, than can be accounted for by the usual theoretical models.

Acknowledgements - The authors would like to acknowledge useful discussions with S.E. Brown. The research of P. Maxton was supported by Associated Western Universities. Work at Los Alamos was performed under the auspices of the U.S. Department of Energy. Work at UCLA was supported in part by National Science Foundation Grant No. DMR 86-20340.

References :

1. S. Forss, J. Raman Spect. **12**, 266 (1982).
2. A. Migliori, P. Maxton, A.M. Clogston, E. Zirngiebl and M. Lowe, Phys. Rev. B **38**, 13464 (1988).
3. P. Maxton, J. Eckert, G. Kwei, A. Migliori and M. Field (in preparation).
4. M. Daurel, P. Delhaes and E. Dupart, Biopolymers **14**, 801 (1975).
5. R.S. Kwok and S.E. Brown, Rev. Sci. Instrum. **61**, 809 (1990).
6. See, e.g., N.W. Ashcroft and N.D. Mermin, *Solid State Physics*, p.499 (Holt, Rinehart and Winston, New York, 1976).
7. G.E. Childs, L.J. Ericks and R.L. Powell, *Thermal Conductivity at Room Temperature and Below*, Natl. Bureau Standards Reference Series **519** (1973).
8. H. J. Simpson Jr and R. E. Marsh, Acta Cryst. **20**, 550 (1966).
9. G. A. Slack, Solid State Phys. **34**, 1 (1979).

