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Specific heat of polysulfur nitride, $(SN)_x$

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Measurements of the specific heat of the crystalline metallic polymer $(SN)_x$ are reported for the temperature range $1.5 \leq T \leq 80$°K. The lattice contribution to the specific heat deviates from Debye behavior near 4°K, changing from T^3 to $T^{2.7}$ and then to a T dependence as temperature increases. The anisotropy in force constants which cause this behavior is discussed in relation to the crystal structure of $(SN)_x$. From the electronic contribution to the specific heat we estimate an electron band-structure density of states at the Fermi level of 0.14 states/(eV spin molecule).

I. INTRODUCTION

During the past several years there has been a considerable experimental and theoretical effort directed towards understanding the properties of polysulfur nitride, $(SN)_x$, the first example of a metallic polymer.[1] The interest in $(SN)_x$ was generated by its apparently one-dimensional structure[2] shown in Fig. 1, a metallic conductivity which is stable against a metal-insulator transition,[3] and the presence of superconductivity below 0.3 °K.[4] More recent work,[5,6] along with the observation of superconductivity, indicates that $(SN)_x$ is a highly anisotropic, but not quasi-one-dimensional, semimetal. As such it is an interesting and unusual system in which to examine both normal-state and superconducting properties.

In this paper we report the specific heat (C) of $(SN)_x$ for the temperature range 1.5–80 °K.[7] In an earlier work[8] three of us had measured the specific heat between 1.5 and 10 °K and found a lattice contribution to C which deviated from isotropic Debye behavior above 4 °K. The purpose of this work is to extend the specific-heat measurements to higher temperatures to determine the nature of the non-Debye behavior. The lattice specific heat of $(SN)_x$ is similar to that of nonconducting polymers, e.g., polyethylene, but differs in its temperature dependence at low temperatures. Our results are consistent with a model of the vibrational spectrum of polymers proposed by Stockmayer and Hecht[9] and examined in detail by Genensky and Newell,[10] in which the specific heat is dominated by the bond-angle-bending force constants of the chain structure. Our results suggest that a large lattice anisotropy exists in addition to electronic anisotropy as determined both experimentally[6] and by band-structure calculations.[5] In addition, a careful search was made for thermal anomalies due to structural or electronic transitions. None were found up to 80 °K, consistent with the absence of a metal-insulator transition in $(SN)_x$.

II. EXPERIMENTAL

Specific-heat measurements between 1.5 and 5 °K were made using a relaxation-time method[11] as described previously.[8] Several single crystals of total mass 25 mg were greased to a silicon thermometer such that the addenda contributed about 10% to the measured heat capacity. The measurements from 5 to 80 °K were also made using the relaxation-time method in a newly developed small sample calorimeter capable of performing both absolute measurements (to ±2–3%) and high-resolution relative measurements (to ±0.1%) on samples as small as a few mg. The sample is bonded to a diamond substrate and the temperature is measured using a thermocouple referenced to a temperature-regulated copper block. The thermocouple output is modulated with a low-temperature

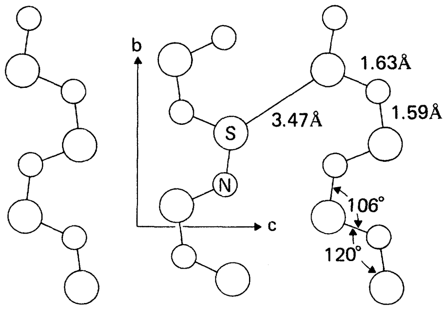

FIG. 1. Chain structure of $(SN)_x$ projected onto $(\bar{1}02)$ plane showing bond lengths and bond angles {after Cohen *et al.* [Ref. 2(b)]}.

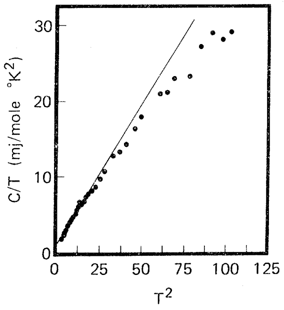

FIG. 2. Specific heat of $(SN)_x$ from 1.5 to 10 °K. Solid line shows least-squares fit to data from 1.5 to 3.2 °K given by $C = \gamma T + \beta T^3$ with $\gamma = 0.83 \pm 0.09$ mJ/mole °K² and $\beta = 0.41 \pm 0.02$ mJ/mole °K⁴.

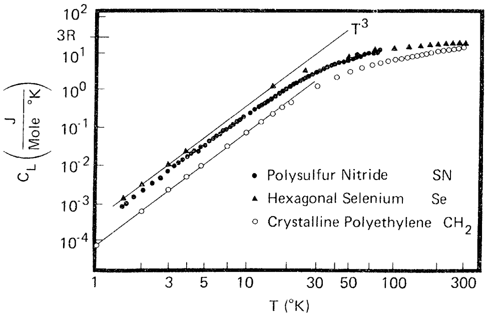

FIG. 4. Lattice specific heat of $(SN)_x$ compared with specific heat of two insulating polymers, hexagonal Se (Ref. 17) and crystalline polyethylene (Refs. 16 and 17).

MOSFET chopper and synchronously demodulated at room temperature. The system incorporates the computer control system designed by Schwall *et al.*,[12] to enable signal averaging and rapid data acquisition. A detailed description of this calorimeter and other examples of its use are given elsewhere.[13]

The crystals used in these measurements are the same ones studied in our earlier low-temperature experiments.[8] Crystals from this batch had a typical room-temperature dc conductivity of 800 $\Omega^{-1}\,\text{cm}^{-1}$, and displayed a conductivity maximum near 20 °K of magnitude $\sigma(20\,°\text{K})/\sigma(300\,°\text{K}) \approx 20$. Details of the preparation and characterization of these and better $(SN)_x$ crystals has been given elsewhere.[1(c),14] It is known that even the best $(SN)_x$ crystals produced to data are imperfect.[2,14,15] Every so-called single crystal is in reality an oriented bundle of fibers with diameters between 200 and 1200 Å. There is also evidence of (100) twinning and molecular scale disorder (manifested by about 10% occupied defect sites).[15] These imperfections cause a 1–3% difference between the x-ray-diffraction-determined-unit-cell density[2(b)] and the experimentally measured density. Although small, this departure from perfect crystallinity may lead to anomalous contributions to the low-temperature specific heat as have been found in other polymers, e.g., polyethylene.[16]

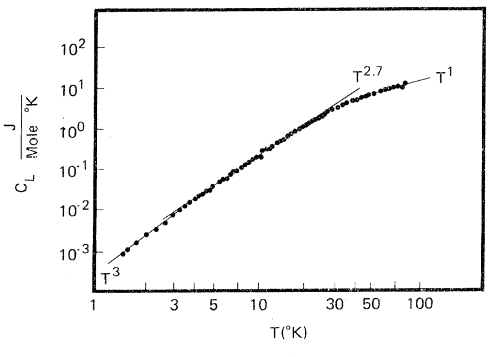

FIG. 3. Lattice specific heat $(C - \gamma T)$ of $(SN)_x$ vs temperature up to 80 °K.

III. RESULTS

Our specific-heat results, corrected for addenda, are presented in Figs. 2 and 3. Figure 2 shows our low-temperature data reported in Ref. 8. The least-squares fit to these data followed the relation $C/T = \gamma + \beta T^2$, with $\gamma = 0.83 \pm 0.09$ mJ/mole °K² and $\beta = 0.405 \pm 0.02$ mJ/mole °K⁴. Figure 3 shows the lattice specific-heat $(C_L = C - \gamma T)$ vs temperature, where we have subtracted the linear electronic contribution determined from Fig. 2. The slope of this logarithmic plot is the temperature exponent (l) of the lattice specific heat (C_L). It is seen that C_L deviates from Debye behavior $(l = 3)$ as low as 3–4 °K and that a wide temperature range exists (4–20 °K) in which the heat capacity follows roughly $T^{2.7}$ dependence. Above this temperature the specific heat begins to saturate toward the classical value for a mole of SN molecules, i.e., $6R \approx 50$ J/mole °K, with a linear dependence between 40 and 80 °K.

Deviation from Debye behavior to a lower value of l is characteristic of a system with anisotropic force constants. This behavior is seen in other polymers as a trend from T^3 dependence at low temperatures to T dependence at high temperatures. To show how the specific heat of $(SN)_x$ differs from that of other polymers, the data for $(SN)_x$ are compared in Fig. 4 with the specific heat of two somewhat similar polymers, hexagonal selenium,[17] and crystalline polyethylene.[16,17] In these materials the T^3 dependence of the specific heat persists up to above 10 °K and then begins to saturate. The unusual aspects of the $(SN)_x$ specific heat are the following:

(i) The lattice specific heat deviates from T^3 behavior at a low temperature (3–4 °K).

(ii) A wide temperature range (4–20 °K) exists in which the temperature exponent of the lattice specific heat lies between 2.5 and 3 (about 2.7). Neither Se nor polyethylene have this temperature behavior.

In the following section these two features will be related to the chain structure of $(SN)_x$.

Further specific-heat measurements on $(SN)_x$ from 0.1 to 1.5 K have been made by Lou and Garito.[18] Their fit to the form $C/T = \gamma + \beta T^2$ gives a value of γ approximately one-half the value we obtain by extrapolating from 1.5 K and a value of β about a factor of 3 greater than obtained from our data. This difference seems rather large and may result in part from errors induced by the strain effects found by Lou and Garito. On the other hand, some of this difference may be due to the concave downward curvature of our data plotted as C/T vs T^2. If we take $\gamma = 0.41$ mJ/mole °K^2 instead of 0.83 mJ/mole °K^2 in calculating the lattice contribution to the specific heat we find that the two sets of data are essentially the same above 5 °K. Thus the temperature dependence of the lattice specific heat as described earlier is not sensitive to the value of γ. At lower temperature the differences are more significant, which suggests that a sample-dependent non-Debye contribution to the specific heat may be present in $(SN)_x$ below 5 °K. Such contributions have been observed in highly crystalline polyethylene and other polymers[16,17] and have been attributed to localized vibrational modes. The magnitude of this non-Debye specific heat is strongly dependent on the degree of crystallinity of the polymer sample. The fibrous morphology and defected nature of $(SN)_x$ crystals discussed above make it plausible that such terms might occur in the $(SN)_x$ specific heat. We have not been able to quantitatively explain this small contribution to C either by including in our fit to the data an Einstein specific-heat function to simulate a localized mode or by observing a hump in a C/T^3 vs T plot of the data as has been found in partially crystalline polyethylene.[16]

Another possible explanation for these results is that the Debye contribution to C only exists below 1.5 °K and the effects of lattice anisotropy are then observed starting at 1.5 °K. This is consistent with the "concave downward" shape of our data. To check this we tried various power-law fits to our data over the temperature range 1.5–10 °K. The best statistical fit gave $C \propto T^{2.5}$ but indicated no linear temperature term. This result seems implausible given the semimetallic nature of $(SN)_x$.

Thus we are faced with some uncertainty in the correct interpretation of our data between 1.5 and 4 °K. It will require a careful measurement of the specific heat between 0.1 and 4 °K, on the same $(SN)_x$ sample, to resolve the questions raised above. Meanwhile, we reemphasize the conclusion reached in Ref. 8, namely, that our results represent upper bounds for the intrinsic values of γ and $1/\beta$.

IV. DISCUSSION

First, we consider the electronic contribution to the specific heat as manifested by our measured low-temperature term γT. From the usual expression,[19] $D(\epsilon_F) = 3\gamma/2\pi^2 k_B(1+\lambda)$, where k_B is Boltzmann's constant and λ is the dimensionless electron-phonon coupling constant, we are able to estimate the band-structure electron state density $D(\epsilon_F)$ at the Fermi surface. With a density of 2.33 g/cm^3 and four SN molecules per unit cell, we find $D(\epsilon_F) = 0.14$ states/(eV spin molecule). We have used the value $\lambda = 0.30$ estimated in Ref. 4 from the McMillan[19] formula for the superconducting transition temperature. Our experimental value for $D(\epsilon_F)$ is in excellent agreement with the theoretical value of 0.13 states/(eV spin molecule) obtained from orthogonalized-plane-wave band-structure calculations.[5]

Now we consider the lattice specific heat. A brief summary of models of polymer specific heat will be given to place the behavior of $(SN)_x$ in perspective. In Fig. 5, several models are summarized in which a structure is specified with particular force constants, from which is derived the phonon density of states $g(\omega)$. The latter determines the specific heat C as a function of temperature. The Debye model [Fig. 5(a)], an isotropic three-dimensional continuum, gives a quadratic phonon density of states, leading to a cubic temperature dependence of the specific heat. This model correctly describes the lattice specific heat of all solids at low enough temperatures,

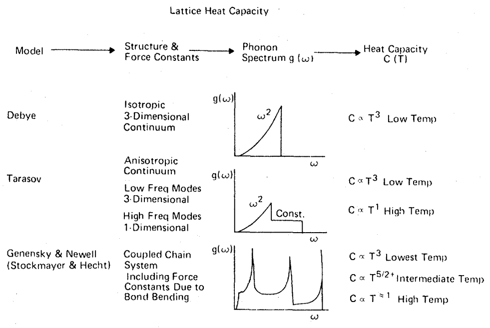

FIG. 5. Summary of various models for the lattice specific heat of solids.

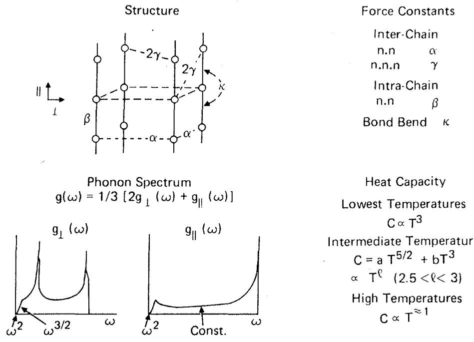

FIG. 6. Structure and interactions assumed in the Genensky-Newell-Stockmayer-Hecht model of the lattice specific heat of a coupled chain system.

where the only excitations are of longer wavelength than any structure in the material.

Measurements of polymer specific heat show a region of linear temperature dependence at high temperatures (around 100 °K). A model proposed by Tarasov[20] [Fig. 5(b)] relates this region to the high-frequency vibrational modes along the chain axis. Thus, a combination of low-frequency three-dimensional modes and high-frequency one-dimensional modes leads to a specific heat proportional to T^3 at low temperatures and changing to T^1 at high temperatures. This parametrization has been successfully used to describe the specific heat of selenium, polyethylene, and other polymers,[16,17] but does not account for the behavior of $(SN)_x$.

A more realistic model of polymer specific heat has been analyzed by Genensky and Newell[10] who found analytical solutions to a model studied numerically by Stockmayer and Hecht.[9] This model is summarized in Fig. 5(c) with the parameters defined in more detail in Fig. 6. In this model, a coupled-chain system is treated within the Born-Von Kármán model including force constants due to nearest neighbors (α, β), next nearest neighbors (γ), and force constants due to bond-angle bending (κ), a significant factor in many polymer systems. This leads to a more-detailed phonon density of states, shown in Fig. 6, and under the condition that the bond-angle-bending force constants dominate the bending response of the chain, the specific heat has the following behavior:

(i) The region of T^3 dependence is suppressed to low temperatures.

(ii) An intermediate temperature range exists in which the heat capacity is a linear combination of $T^{2.5}$ and T^3 dependence, giving a temperature exponent between 2.5 and 3.

(iii) At high temperatures, the specific heat tends to linear dependence and eventually saturates in agreement with the Tarasov model.

The conditions under which this behavior occurs are illustrated in Fig. 6. There are two primary types of vibrational modes, parallel to the chain axis and perpendicular to the chain axis. The modes parallel to the chain behave normally because the magnitude of κ does not enter these modes. They correspond to the high-frequency one-dimensional modes in the Tarasov model, and contribute a cubic term in the specific heat at low temperature and a linear term at high temperature.

The major difference from the Tarasov model occurs in the perpendicular modes. Under the condition that the bond-angle force constants κ dominate these modes, an intermediate frequency range results with a different dispersion relation, contributing a $T^{2.5}$ dependence to the specific heat. In the appropriate temperature range the temperature exponent of specific heat is thus a linear combination of 2.5 and 3, and the purely cubic temperature range is suppressed to lower temperature. If the magnitude of κ is comparable to or smaller than α, γ, the behavior reverts to the simpler Tarasov model, with no region of unusual temperature dependence.

As noted earlier, Fig. 3 shows that the exponent of the lattice specific heat changes from 3.0 to 2.7 and then to 1.0 with increasing temperature. The Debye temperature associated with the cubic region is given by

$$\Theta_D^3 = \tfrac{2}{3}(\pi^4 12R/5)(1/\beta) .$$

The factor of $\frac{2}{3}$ arises because the branch with displacements in the z direction does not contribute, since $\beta \gg \alpha, \gamma$. Using our experimental value of β this expression gives $\Theta_D = 148$ °K (102 cm^{-1}) which is interpreted as the characteristic energy associated with interchain coupling. This is comparable, but less than, the magnitude of the interchain coupling found in Se. Recent studies of the ir and Raman spectra[21] and preliminary neutron scattering experiments[1(b)] in $(SN)_x$ give other, rather similar estimates, for the interchain coupling. The value of β found by Lou and Garito[18] gives a result for Θ_D of 103 °K, suggesting somewhat weaker interchain coupling. Both values for Θ_D show that non-negligible level of lattice interchain interaction exists. The insolubility of $(SN)_x$ and its resistance to intercalation are further evidence of important interchain interactions. In summary, our results show that, from a lattice point of view, $(SN)_x$ is a strongly anisotropic material with a force constant distribution somewhat more anisotropic than selenium.

From the above discussion it is clear that the behavior of the lattice specific heat of $(SN)_x$ may be accounted for by the model of Genensky and Newell. Detailed confirmation of this interpretation will require studies of the vibrational modes of $(SN)_x$ through neutron scattering experiments, elastic-constant measurements, or other techniques which yield less of a macroscopic average than the heat capacity. The condition to be verified is that the bond-angle-bending force constant κ dominates the perpendicular modes of the crystal in the temperature region around 5–20 °K. Referring to the structure of $(SN)_x$ in Fig. 1, it is clear that the chains are not simple linear arrays, but consist of a cis-trans arrangement of sulfur and nitrogen atoms. It seems likely that the explanation for the unusual temperature dependence of the lattice specific heat of $(SN)_x$ lies in the dominance of the bond-angle force constants in this cis-trans structure. The relationship of this type of lattice anisotropy to other properties such as the occurrence of superconductivity and the temperature[22,23] and pressure dependence[24] of the normal conductivity is yet to be understood.

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