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Low-Temperature Specific Heat of Polysulfur Nitride, $(SN)_x$

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Measurements of the specific heat of crystalline $(SN)_x$ in the region 1.5–10°K are reported. A linear temperature contribution to the specific heat is found and interpreted as arising from an electron state density of 0.18 state/(eV spin molecule) and a one-dimensional tight-binding conduction band of width ≥ 0.9 eV. Analysis of the lattice specific-heat contribution supports existing evidence that $(SN)_x$ is a highly anisotropic crystalline polymer and suggests a possible explanation for the apparent absence of a Peierls transition.

Much attention is currently being directed toward the study of conducting one-dimensional (1-D) systems.[1,2] Recently, Walatka, Labes, and Perlstein[3] (WLP) have suggested that the crystalline polymer polysulfur nitride, $(SN)_x$, may be another example of a 1-D conductor. They have reported metallic levels of dc electrical conductivity in $(SN)_x$ over the temperature range 4.2–300°K, in contrast to all other known 1-D conductors in which a metal-insulator transition occurs within this same temperature region. This exciting result clearly demonstrates that further studies on the properties of $(SN)_x$ are important for understanding the nature of 1-D conductors and should lend insight into ways to stabilize the metallic state in present and future 1-D materials. In pursuit of this objective, we report here the first specific-heat measurements on $(SN)_x$. These results, along with conductivity, thermopower, and magnetic-susceptibility data on our crystals, indicate that metallic behavior in $(SN)_x$ persists at temperatures down to 1.5°K. Our data enable an estimate of ~0.9 eV for the conduction-band width to be made on the basis of a simple 1-D tight-binding model. Moreover, the dependence of specific heat on temperature above 3.2°K gives clear evidence for the importance of anisotropic force constants in $(SN)_x$. An analysis of these data leads us to suggest that the Peierls transition may be suppressed by fluctuations in

$(SN)_x$ because of weak interchain coupling.

Our samples were prepared in a manner similar to that described by WLP except that unpolymerized S_4N_4 and S_2N_2 were removed from the $(SN)_x$ by resublimation rather than by washing with benzene. The S_4N_4 starting material, carefully purified by recrystallization followed by gradient sublimation, was stored under vacuum before using. Chemical analysis of the resulting brass-colored $(SN)_x$ crystals indicated N, 29.60; S, 69.61 (calculated, N, 30.41; S, 69.59). The only other element found in a specific analysis was hydrogen [(0.2 ± 2)% by weight]. X-ray measurements on compressed samples agreed with the known x-ray structure[4] of $(SN)_x$ and gave no indication of S_4N_4 or S_2N_2 inclusions. Our x-ray data also gave no evidence of noncrystalline phases. Full details of the preparation and characterization of our $(SN)_x$ crystals will be presented elsewhere.

In order to compare our samples directly with those of WLP, we have performed conductivity and thermopower measurements between 1 and 300°K. The conductivity along the fibrous direction (each crystal being a bundle of parallel fibers) was measured by using a standard four-probe ac technique.[5] Typical room-temperature conductivities (σ_{RT}) averaged 600 $(\Omega\ cm)^{-1}$ with considerable variation among samples, it being difficult to accurately determine the cross-sec-

tional area of the fibrous bundle. A small conductivity maximum, varying between 20 and 31°K in position and between 6 and 25 in conductivity ratio $\sigma_{peak}/\sigma_{RT}$, was observed in all samples. For any given sample, the lower in temperature the conductivity peak, the higher the ratio $\sigma_{peak}/\sigma_{RT}$. In the interval 1–4°K the conductivity varied only slightly with temperature and was always significantly greater than at 300°K. The results above differ quantitatively from those of WLP who found the peak in σ to be at 33°K and $\sigma_{peak}/\sigma_{RT} \lesssim 5$ in all their samples. Our thermopower data qualitatively follow the WLP results with the additional observation of a negative peak (~ 4 μV/°K) near the conductivity maximum. Between room temperature and 8°K (our measurement limit) the thermopower is $\leqslant 6$ μV/°K, suggestive of metallic behavior. We noted no change in transport properties upon temperature cycling. The underlying cause of the conductivity maximum and thermopower peak is at present uncertain and may be different than that of other 1-D conductors. On the other hand the conductivity behavior could result from a nonideal Peierls transition.[6]

The specific heat was measured between 1.5 and 10°K by using a relaxation-time method.[7] Several single crystals of total mass 25 mg were greased to a silicon thermometer with the addenda contributing about 10% to the total measured heat capacity. Figure 1 shows the resulting $(SN)_x$ specific heat. The best least-squares fit to the data below 3.2°K followed the relation $C/T = \gamma + \beta T^2$, with $\gamma = (18.0 \pm 2.0) \times 10^{-6}$ J/g °K^2, $\beta = (8.8$

$\pm 0.4) \times 10^{-6}$ J/g °K^4. This is shown in Fig. 2. An extrapolation of this fit above 3.2°K is shown in Fig. 1, displaying a significant departure from the actual data. A fit to the data above 3.2°K was made with a relation of the form $C - \gamma T = AT^n$ for which we found $n = 2.7$ using γ from the low-temperature analysis.

We will defer discussion of the high-temperature results and direct our immediate attention to the specific heat below 3.2°K. Faced with the high conductivity in this range, we must conclude that a major portion, if not all, of the observed linear term is metallic in origin. This linear contribution amounts to about 50% of the total sample specific heat at 1.5°K and about 18% at 3.2°K. Assuming γ to be entirely electronic, we are able to estimate the electron state density $D(\epsilon_F)$ at the Fermi surface via the relation $D(\epsilon_F) = 3\gamma/2\pi^2 k$, where k is Boltzmann's constant. Using a density of 2.33 g/cm^3 and four SN molecules per unit cell,[4] we find $D(\epsilon_F) = 0.18$ state/(eV spin molecule).

WLP discuss a simplified 1-D band model based on π overlap between SN groups along the polymeric chain. By expressing this model in tight-binding formalism, we obtain a relation for the conduction-band width given by $E_w = 1/\pi v_a D(\epsilon_F)$ $\times [\mathcal{E}_F(1 - \mathcal{E}_F)]^{1/2}$, where v_a is the unit-cell volume and $\mathcal{E}_F$ is the band filling factor. Since there is one extra π electron per SN group, we will as-
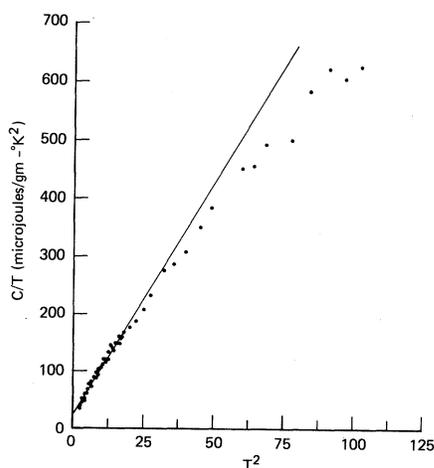

FIG. 1. Specific heat of crystalline $(SN)_x$ plotted as C/T versus T^2 between 1.5 and 10°K. Corrections have been made for the approximately 10% addenda. The fit to the data below 3.2°K is shown by the solid line. The data shown are from three different runs.
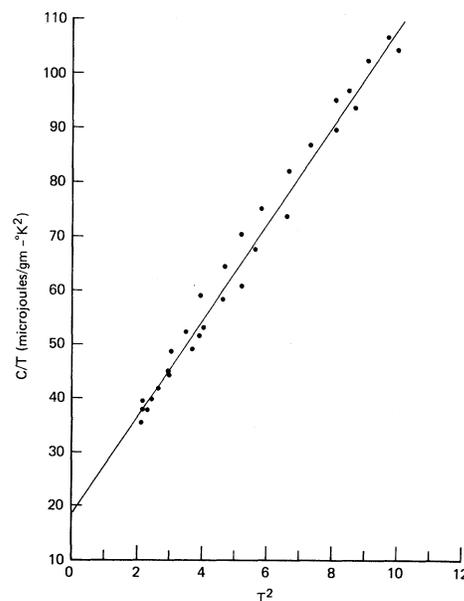

FIG. 2. Details of $(SN)_x$ specific heat below 3.2°K. A fit with the equation $C/T = \gamma + \beta T^2$ yielded $\gamma = (18.0 \pm 2.0) \times 10^{-6}$ J/g °K^2 and $\beta = (8.8 \pm 0.4) \times 10^{-6}$ J/g °K^4.

sume a half-filled conduction band, i.e., $\mathcal{E}_F = \frac{1}{2}$. Thus, from our value for $D(\epsilon_F)$ obtained from the linear term in the specific heat, we find $E_w = 0.9$ eV. Because the effect of including the electron-phonon interaction γ in the theory of electronic specific heat is to increase the measured γ $[\gamma \sim D(\epsilon_F)(1+\lambda)]$, our bandwidth estimate above represents a lower bound pursuant to other constraints of the model.[8] Even this lower-bound estimate of the bandwidth is larger than that of the best known organic conductor $(E_w \sim 0.5$ eV$)$,[1] implying greater overlap of molecular orbitals along the $(SN)_x$ chain than along the stacking direction of the TCNQ salts.

Measurements of magnetic susceptibility, ESR, and optical reflectivity are also consistent with metallic behavior in $(SN)_x$. DiSalvo[9] found the susceptibility to be negative and constant from 4 to 300°K and equal to -0.3×10^{-6} emu/g. Estimating the diamagnetic core contribution from either Pascal's constants or the measured value for S_4N_4,[10] we find it plausible that $(SN)_x$ may contain a small temperature-independent paramagnetic susceptibility of order 0.2×10^{-6} emu/g. Interpreted as a Pauli term $[\chi = 2\mu_B{}^2 D(\epsilon_F)]$ this yields an electron state density of about 0.14 state/(eV spin molecule) which is close to our specific-heat value.[11] ESR data taken on our samples by Mehran[12] from 2 to 300°K showed no resonance structure, a common result for many metals. In addition, preliminary optical reflectivity results on polycrystalline films of $(SN)_x$ show a Drude-like plasma edge near 2.8 eV.[13]

We now turn our attention to the specific-heat data above 3.2°K. From a Debye analysis of the T^3 term found below this temperature, we obtain 170°K for the Debye temperature (Θ_D), treating S and N as separate atoms. However, as seen in Fig. 1, the data above 3.2°K have a weaker than T^3 dependence and are found to behave more like $T^{2.7}$. Such deviations from the strict T^3 law are always found in systems with anisotropic force constants, examples being graphite, selenium, and polyethylene among others.[14] A study of Boudeulle's[4] complete crystal structure suggests that, from a force-constant point of view, solid $(SN)_x$ may be considered as a collection of weakly coupled 1-D chains. Several lattice-dynamical models have been proposed for such chain-polymer crystals.[14] Of these we find the analytic solution of Genensky and Newell[15] to best describe our data. Briefly summarized, their findings show a cubic dependence at very low temperatures of the form $C \propto (T/T_m)^3$, where T_m

is the temperature equivalent to the maximum frequency for phonons along the polymeric chain (analogous to Θ_D in isotropic systems). At slightly higher temperatures they find the lattice specific heat to vary as $T^{2.5}$, a temperature dependence which results from the dominance of the bending moment constant between units along the polymer chain. In yet higher temperature ranges, T^2, $T^{1.5}$, and T dependencies are predicted. Preliminary results[16] on our crystals at higher temperatures show that $C \sim T^{2.5}$ between 6 and 30°K, with a weaker temperature dependence above 30°K. Thus, our data strongly support the view that $(SN)_x$ is a quasi-one-dimensional solid, at least from a lattice-dynamics point of view. A more thorough discussion of these high-temperature results will be given elsewhere.

These results suggest one possible explanation for the apparent absence of a Peierls transition in $(SN)_x$. It is known[6] that in a strictly 1-D system no Peierls transition is observable because fluctuations suppress the actual transition temperature to zero [the mean-field transition still occurs at a higher temperature (T_p)]. If, however, one allows for some interchain interaction (surely present in real systems) then a transition is observable at a finite temperature $(T_{3D} < T_p)$ determined by the strength of the interaction. We assume here that we are still in the limit where the interchain transfer integral $(t_\perp)$ is very much smaller than the intrachain transfer integral[17] $(t_{||})$. Our specific-heat results show that $(SN)_x$ has much weaker lattice forces between chains than other 1-D conductors. We infer this from the fact that the departure from T^3 behavior begins at a lower temperature[18] in $(SN)_x$. Thus, if the electronic interactions are as anisotropic as the lattice forces which determine the specific heat, we can understand the apparent absence of a Peierls transition (T_{3D}) above 1°K on the basis of a weak interchain interaction. Obviously, without more direct information, this idea is quite speculative. Experiments to determine if fluctuation effects are observable at low temperature and to look for a Peierls transition below 1°K are in progress. We cannot determine with our present data the extent of disorder along the polymer chain, the role of impurities or defects, the extent of chain crosslinking, or the magnitude of $t_\perp/t_{||}$. If any of these effects are large, they would also tend to suppress the observable Peierls transition (T_{3D}).

In conclusion, we have discussed specific-heat, conductivity, thermopower, magnetic-suscepti-

bility, and ESR data which substantiate the existence of a metallic state in $(SN)_x$ down to at least 1.0°K. Interpreting the linear term on the basis of a tight-binding model results in a conduction-band width estimate of 0.9 eV. Consideration of the lattice contributions to the specific heat suggests that $(SN)_x$ is a highly anisotropic crystalline polymer.

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[8]Other physical mechanisms, such as impurity banding and disorder, can give rise to a linear term in the low-temperature specific heat. Although these causes represent possible explanations for our results, we feel that current lack of evidence for their existence in $(SN)_x$ justifies our use of the metallic interpretation for γ. Note that if we assume only part of the contribution to γ is of metallic origin then an even larger estimate of the bandwidth results from our tight-binding model. Experiments to lower temperature (< 1.5°K) are in progress to determine the metallic contribution more accurately.

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[13]P. M. Grant, private communication; A. J. Heeger, private communication. We find that the tight-binding model used above, with $n = 3.05 \times 10^{22}/cm^3$ and 3.08 Å as the center-to-center distance between SN pairs (Ref. 4), gives $E_w \sim 0.5$ eV. Although they differ from our specific-heat result, we note that bandwidths calculated from plasma energies depend inverse quadratically on the molecular separation. Such a separation may be difficult to define uniquely in a material like $(SN)_x$ and we shall have to await satisfactory band-structure calculations before relating the optical results to the specific heat.

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[18]In the TCNQ salts and $K_2[Pt(CN)_4]Cl_{0.3} \cdot 3H_2O$, no deviation from T^3 behavior such as we find in $(SN)_x$ has been observed up to 6°K, the present measurement limit. Recently, P. Delhaes, to be published, has found in quinolinium-TCNQ salt $Q(TCNQ)_2$ a departure from T^3 starting near 20°K and such would probably be typical of most TCNQ salts.