

electron kinetic energy. And also, to recover the kinetic energy, further acceleration around the torus would be effective as proposed by Rostoker.<sup>3</sup>

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<sup>1</sup>G. I. Budker, in *Proceedings of the CERN Symposium on High-Energy Accelerators and Pion Physics, Geneva, Switzerland, 1956* (CERN Scientific Information Service, Geneva, Switzerland, 1956) Vol. 1, p. 68.

<sup>2</sup>G. S. Janes, R. H. Levy, H. A. Bethe, and B. T. Feld, *Phys. Rev.* **145**, 925 (1966).

<sup>3</sup>N. Rostoker, *Particle Accel.* **5**, 93 (1973).

<sup>4</sup>N. C. Christofilos, in *Proceedings of the Second International Conference on the Peaceful Uses for Atomic Energy, Geneva, Switzerland, 1958* (United Nations, Geneva, Switzerland, 1958), Vol. 32, p. 279.

<sup>5</sup>S. Yoshikawa and N. C. Christofilos, in *Plasma*

*Physics and Controlled Nuclear Fusion Research* (International Atomic Energy Agency, Vienna, 1971), Vol. 2, p. 357.

<sup>6</sup>For example, C. Ekdahl, M. Greenspan, R. E. Kribel, J. Sethian, and C. B. Wharton, *Phys. Rev. Lett.* **33**, 346 (1974).

<sup>7</sup>*Phys. Today* **21**, No. 2, 51 (1968).

<sup>8</sup>J. Benford, B. Ecker, and V. Bailey, *Phys. Rev. Lett.* **33**, 574 (1974).

<sup>9</sup>P. Gilad, B. R. Kusse, and T. R. Lockner, *Phys. Rev. Lett.* **33**, 1275 (1974).

<sup>10</sup>N. C. Christofilos, W. C. Condit, Jr., T. J. Fessenden, R. E. Hester, S. Humphries, G. D. Porter, B. W. Stallard, and P. B. Weiss, in *Plasma Physics and Controlled Nuclear Fusion Research* (International Atomic Energy Agency, Vienna, 1971), Vol. 1, p. 119; R. J. Briggs, G. D. Porter, B. W. Stallard, J. Taska, and P. B. Weiss, *Phys. Fluids* **16**, 1934 (1973).

<sup>11</sup>J. J. Bzura, T. J. Fessenden, H. H. Fleischmann, D. A. Phelps, A. C. Smith, Jr., and D. M. Woodall, *Phys. Rev. Lett.* **29**, 256 (1972).

<sup>12</sup>Y. Hamada and A. Mohri, *Jpn. J. Appl. Phys.* **13**, 1624 (1974).

<sup>13</sup>B. Bernstein and I. Smith, *IEEE Trans. Nucl. Sci.* **20**, No. 3, 294 (1973).

<sup>14</sup>R. H. Levy, J. D. Daugherty, and O. Buneman, *Phys. Fluids* **12**, 2616 (1969).

## Superconductivity in Polysulfur Nitride (SN)<sub>x</sub>

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The inorganic crystalline polymer polysulfur nitride has been found to become superconducting with a transition temperature of  $(0.26 \pm 0.03)^\circ\text{K}$ .

We have discovered that the crystalline polymer polysulfur nitride (SN)<sub>x</sub> becomes superconducting with a transition temperature of  $(0.26 \pm 0.03)^\circ\text{K}$ . This is the first polymeric system known to exhibit superconductivity. The present experimental information about (SN)<sub>x</sub> indicates that it is a quasi-one-dimensional (1D) material. As such it should prove to be a model system for studying quasi-1D superconductivity in the same way that the layered dichalcogenides and their intercalation compounds have been model systems for quasi-two-dimensional superconductivity.<sup>1</sup> In addition, we note that (SN)<sub>x</sub> involves elements

from a region of the periodic table which previously has shown no superconductivity at zero pressure. This suggests that superconductivity is even more widespread than presently believed. Although we have no reason to doubt that the superconductivity observed in (SN)<sub>x</sub> obeys the conventional BCS theory, the polymeric structure of (SN)<sub>x</sub>, with suitable modification, may allow one to test the excitonic theory of superconductivity proposed by Little.<sup>2</sup> Furthermore, a more detailed study of (SN)<sub>x</sub> should help clarify the present theoretical uncertainty about the conditions under which quasi-1D systems become Peierls

insulators or superconductors.<sup>3</sup>

Conductivity ( $\sigma$ ) measurements were made along the fiber axis on three samples, all of which showed superconductivity below 0.3°K. The room temperature  $\sigma$  was typically  $1000 \Omega^{-1} \text{cm}^{-1}$ , a small resistivity minimum was observed between 20 and 30°K, and  $\sigma_{RT}/\sigma_{1^\circ K}$  was  $\sim 0.2$ . Between 1°K and the onset of superconductivity,  $\sigma$  is constant, presumably being dominated by impurity or defect scattering. The transitions for the three samples occurred at about 0.28, 0.25, and 0.26°K, respectively.<sup>4</sup> The transition for one of the samples is shown in Fig. 1, at both earth magnetic field and at 335 G.<sup>5</sup> *The decrease in the transition temperature ( $T_c$ ) with increasing magnetic field is the most conclusive evidence that superconductivity has been observed.* Detailed studies of the magnetic-field ( $H$ ) dependence of  $T_c$  will be presented elsewhere. Our preliminary measurements indicate that the depression of  $T_c$  is significantly less when  $H$  is parallel to the fiber axis than when  $H$  is perpendicular to it. The transition is rather broad ( $\Delta T_c \sim 0.08^\circ\text{K}$ , suggesting that disorder, defects, or impurities are limiting  $\Delta T_c$  and possibly even  $T_c$ ). Fluctuation effects may also contribute to  $\Delta T_c$  but better quality samples are needed before this can be convincingly tested.<sup>6</sup>

One sample showed a small but measurable resistivity well below  $T_c$ . In addition, the critical currents observed in all samples were orders of magnitude lower than would be predicted by Sils-

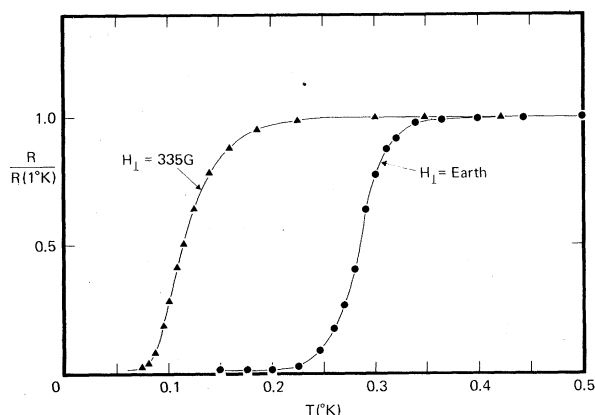


FIG. 1. Temperature-dependent resistance of one  $(\text{SN})_x$  crystal along the fiber axis normalized to  $R(1^\circ\text{K})$  with the earth's magnetic field and with 335 G applied perpendicular to the fiber axis. The conductivity at 1°K is  $\sim 5000 \Omega^{-1}$ ; below the transition (at 0.07°K)  $\sigma$  is  $> 5 \times 10^6 \Omega^{-1} \text{cm}^{-1}$  (this value being our instrumental limit).

bee's rule. Both of these results indicate that the superconductivity is very filamentary with the possibility of weak links in some samples. The large magnetic field needed to suppress  $T_c$  and the estimated short electron mean free path (see below) also suggest filamentary or type-II superconductivity. Heat-capacity and magnetization studies are in progress to determine if the observed superconductivity is a bulk property.

Polysulfur nitride has been known for many years but has only recently become available in a highly crystalline form. Studies of the conductivity,<sup>7</sup> specific heat,<sup>8</sup> optical reflectivity,<sup>9</sup> and magnetic susceptibility<sup>10</sup> have recently been reported. The degree of anisotropy is not accurately known at present. Single crystals exhibit marked anisotropy in the reflection of polarized light, in conductivity, and in their critical-field behavior. However, the recent crystal-structure determination by Boudeulle<sup>11</sup> indicates that some interchain interaction could occur because the S-S distance between chains in the  $(\bar{1}02)$  plane is 3.10 Å (smaller than the van der Waals spacing of  $\sim 3.5$  Å). We note that along the polymer axis ( $b$  crystalline axis) the sulfur and nitrogen atoms form alternating covalent bonds of lengths 1.58 and 1.72 Å. Molecular-orbital and band-structure calculations<sup>12</sup> now in progress should help clarify the degree of anisotropy and its effect on the unusual properties of  $(\text{SN})_x$ .

The preparation and characterization of our  $(\text{SN})_x$  crystals was described previously.<sup>8</sup> Chemical analysis of our samples shows that the total impurity level is less than 0.5 at.%. Our x-ray data indicate that our samples are a single phase. Apparently,  $(\text{SN})_x$  crystals can be grown in two forms with different visual appearance, characterized by Labes and co-workers<sup>7</sup> as "more-fibrous" and "less-fibrous." The crystals studied in this work appeared to be of the more-fibrous type; each crystal studied consisted of an oriented bundle of fibers. We estimate the individual fibers to be less than 1  $\mu\text{m}$  in diameter. The samples were measured by an ac (20 Hz) four-probe method using silver paste contacts. Typical sample size was 1.5 mm  $\times$  0.1 mm  $\times$  0.05 mm. Considerable care was taken to avoid the problems associated with four-probe measurements on anisotropic systems. The absence of phase changes as a function of  $T$  in our ac signal and consistent readings in various nested and unnested probe configurations convince us that the conductivity we measure is not caused by spurious anisotropy effects. Temperatures between 4 and 0.07°K were

obtained with a dilution refrigerator. The temperature was measured with two Speer 220- $\Omega$  resistors cemented close to the sample holder. The samples were mounted on alumina integrated-circuit chips with four short gold wires (0.002-in. diam). The measured conductivity was reproducible after many thermal cycles.

From the 1D tight-binding relation  $l = \sigma\pi\hbar/2Ne^2a$  we estimate the mean free path ( $l$ ) to be less than 15 Å at 2°K. This would suggest we are in the dirty limit of superconductivity. From the Mc-Millan<sup>13</sup> formula for  $T_c$  and the Debye temperature of 170°K obtained from specific-heat data,<sup>8</sup> we estimate the electron-phonon coupling constant ( $\lambda$ ) to be  $\lambda = 0.31$ . This agrees surprisingly well with a much cruder estimate made previously<sup>8</sup> from the free-electron contribution to the specific heat and magnetic susceptibility.

In summary, we have established conclusively that superconductivity occurs in the polymeric system (SN)<sub>x</sub>. This opens up the exciting possibility of studying superconductivity in a quasi-1D system. Obviously, many important facts must first be determined. The degree of one-dimensionality in (SN)<sub>x</sub> remains an open question. The quality of the crystals must be improved since it is possible that  $T_c$  for a pure, highly ordered crystal of (SN)<sub>x</sub> could be considerably higher than 0.26°K. On the other hand, experiments to determine if the observed superconductivity is a bulk property must be done.

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<sup>1</sup>F. R. Gamble and T. H. Geballe, in *Treatise of Solid State Chemistry*, edited by N. B. Hannay (Plenum, New York, 1974); A. D. Joffe, in *Festkörperprobleme*, edited by H.-J. Queisser (Pergamon, New York, 1973), Vol. 13.

<sup>2</sup>W. A. Little, Phys. Rev. **134**, A1416 (1964).

<sup>3</sup>See, for example, H. Gutfreund, B. Horovitz, and M. Weger, J. Phys. C: Proc. Phys. Soc., London **7**, 383 (1974); M. J. Rice and S. Strässler, Solid State Commun. **13**, 697 (1973); K. Levin, D. L. Mills, and S. L. Cunningham, Solid State Commun. **15**, 705 (1974).

<sup>4</sup>This difference in  $T_c$  is most likely a sample-dependent effect but could result from different thermal contact between the various samples and the dilution refrigerator.

<sup>5</sup>The value of magnetic field at the sample position is not accurately known. We estimate the actual field is within 10% of the applied field of 335 G.

<sup>6</sup>Attempts to fit the well-known relations for paraconductivity in one, two, and three dimensions did not give meaningful results. Given the highly disordered nature of our (SN)<sub>x</sub> crystals, we would expect most of the line-width to be caused by sample inhomogeneity.

<sup>7</sup>V. V. Walatka, M. M. Labes, and J. H. Perlstein, Phys. Rev. Lett. **31**, 1139 (1973); C. H. Hsu and M. M. Labes, J. Chem. Phys. **61**, 4640 (1974).

<sup>8</sup>R. L. Greene, P. M. Grant, and G. B. Street, Phys. Rev. Lett. **34**, 89 (1975).

<sup>9</sup>P. M. Grant and G. B. Street, to be published; A. A. Bright, M. J. Cohen, A. F. Garito, A. J. Heeger, C. M. Mikulski, P. J. Russo, and A. G. MacDiarmid, Phys. Rev. Lett. **34**, 206 (1975).

<sup>10</sup>F. J. Di Salvo, V. V. Walatka, and M. M. Labes, unpublished; A. J. Heeger, private communication; Ref. 9.

<sup>11</sup>M. Boudeulle and P. Michel, Acta Crystallogr., Sect. A **28**, S199 (1972); M. Boudeulle, Ph.D. thesis, University of Lyon, 1974 (unpublished).

<sup>12</sup>A. Zunger, to be published; W. Rudge, to be published; W. I. Friesen, A. J. Berlinsky, B. Bergensen, L. Weiler, and T. M. Rice, to be published.

<sup>13</sup>W. L. McMillan, Phys. Rev. **167**, 331 (1968). We assume that  $\mu^* = 0.1$ .