Pressure Dependence of Superconductivity and Normal Conductivity in Polymeric Sulfur Nitride, $(SN)_x$

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The hydrostatic pressure dependence of the superconducting transition temperature T_c, the critical magnetic field H_{c2}, and the normal-state conductivity of crystalline $(SN)_x$ are reported. Under pressure T_c increases from 0.33°K ($P=0$) to 0.54°K ($P=9\pm1$ kbar). The increase in T_c is attributed to pressure-induced band-structure changes.

Recently, Greene, Street, and Suter[1] reported observing superconductivity in crystals of poly sulfur nitride, $(SN)_x$. This material was already the subject of considerable interest because of its quasi-one-dimensional metallic properties.[2-4] The superconductivity was notable as it was the first observation of superconductivity in a polymeric material and the first report of superconductivity at atmospheric pressure from columns V and VI of the periodic table. Because of the large anisotropy in the properties of $(SN)_x$, a detailed understanding of the superconductivity becomes of particular interest. In this Letter we report the first measurements of the effects of hydrostatic pressure on the superconductivity and the normal conductivity[5] in $(SN)_x$ crystals. Pressure is found to increase the superconducting transition temperature T_c, an unusual effect among known nontransition metal superconductors. We show that this anomalous behavior, the increase in normal-state conductivity, and the critical magnetic field behavior, can be qualitatively understood as arising from electronic band-structure changes under pressure.

Pressure measurements were carried out in a beryllium-copper clamped piston and cylinder device[6] using n-heptane as the pressure medium. Pressure was applied at room temperature resulting in quasi-hydrostatic-pressure conditions for the low-temperature experiments. Measurements were made on several batches of $(SN)_x$ crystals prepared under different conditions. Pressure effects on the room-temperature conductivity were found to be the same for all batches. Results reported in this Letter are for material prepared by an improved technique published elsewhere[7] resulting in crystals with superior electrical properties to those reported earlier.[1-4] The most notable improvements in the properties of these crystals are increased room-temperature conductivity, increased conductivity ratio $\sigma(4°\mathrm{K})/\sigma(300°\mathrm{K})$ from ~20 to >100, and increased T_c from 0.26 to 0.33°K.

Superconductivity was detected by a four-probe resistance measurement along the crystallographic b axis using the same experimental techniques as were used in the atmospheric-pressure measurements.[1] The pressure dependence of T_c is shown in Fig. 1 for pressures up to 9 kbar. Error bars on pressure are necessarily large because of the large volume change on freezing and subsequent cooling of heptane and the unknown, but presumably highly anisotropic, elastic properties of $(SN)_x$. The pressure dependence of T_c, which is nonlinear, can be adequately expressed with a quadratic term as indicated in Fig. 1. We attach no physical significance to this fit. The

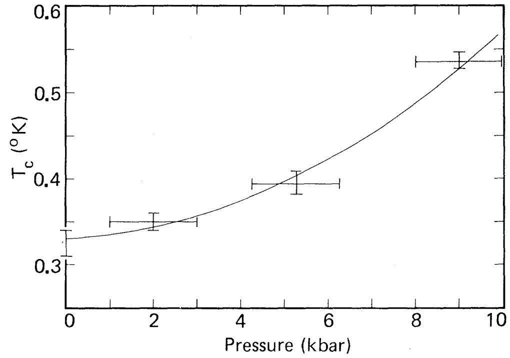

FIG. 1. Pressure dependence of the superconducting transition temperature T_c for $(SN)_x$ crystals. The solid line is the fit by the empirical relation $T_c=0.33+3.0\times10^{-6}P+2.1\times10^{-9}P^2$, where P is in bars.

width of the transition ($\Delta T_c = 0.05$°K) increased with pressure, approximately doubling at $P = 9$ kbar. Because of the quasi-hydrostatic pressure conditions, this broadening is not considered intrinsic, but rather is indicative of pressure inhomogeneities.

Measurements were also made of the critical magnetic field H_{c2} (for $H \leq 300$ Oe) with H perpendicular to the b axis. A detailed report will be presented elsewhere; however, a few preliminary observations can be made now. First, we find that $|\partial H_{c2}/\partial T|_{T_c}$ decreases linearly with pressure from 1700 Oe/°K at $P = 0$ to 900 Oe/°K at $P =$ = 9 kbar. It can be shown[8] that $|\partial H_{c2}/\partial T|_{T_c} \propto 1/v_F$, where v_F is the Fermi velocity averaged over directions parallel and perpendicular to the b axis. In a tight-binding model one expects $v_F \propto t$ (average transfer integral), and hence our data are consistent with an increase of t with pressure. This is certainly not unexpected since overlap between chains must increase significantly with pressure. Secondly, when our high-pressure data are compared with the atmospheric-pressure $H_{c2\perp}$ data of Azevedo *et al.*[9] they suggest that $H_{c2\perp}$ ($T = 0$°K) decreases with pressure. Since $H_{c2\perp}(0) \propto T_c/v_F$, this is also consistent with an incresing transfer integral.

The effects of pressure on the normal conductivity ($T = 295$°K) parallel and perpendicular to the b axis (fiber axis) are shown in Fig. 2. These results were obtained using the Montgomery geometry[10] to obtain both conductivity components on a single sample. The parallel conductivity, $\sigma_{\parallel}$, obtained from the analysis of the Montgomery data (points on Fig. 2) is in excellent agreement with results on a typical sample using a linear four-probe geometry (solid line on Fig. 2). Despite radically different temperature dependences of $\sigma_{\parallel}$ and $\sigma_{\perp}$,[2,11] their pressure dependences ($T = 295$°K) are very similar, increasing exponentially below 4 kbar and tending to saturation at about 12 kbar. Results were reproducible, and no hysteresis was observed on repeated pressure cycling.

As temperature is decreased the conductivity anisotropy $\sigma_{\parallel}/\sigma_{\perp}$ at atmospheric pressure increases strongly from about 200–400 at 300°K to about 5×10^4 at 4°K.[11] This increase is mainly due to the approximately hundredfold increase in $\sigma_{\parallel}$, with $\sigma_{\perp}$ only decreasing by about a factor of 2 over this temperature range. Under 10-kbar pressure $\sigma_{\parallel}/\sigma_{\perp}$ decreases by a factor of 2 at 295°K and by a factor of 4 at 4°K.

The application of pressure to a solid can lead to changes in both electronic band structure and the phonon spectrum. Based on our current knowledge of the properties of $(SN)_x$ we believe that band-structure changes under pressure are the primary reason for the observed increase in T_c and the normal-state conductivity.

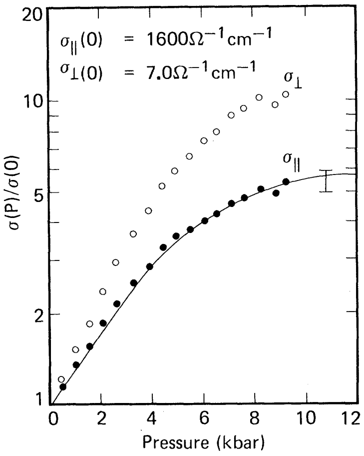

FIG. 2. Pressure dependence of the normal conductivity of $(SN)_x$ at $T = 295$°K. Data points are for a Montgomery-geometry crystal. The solid line is the component of conductivity parallel to the b axis from a typical linear four-probe measurement. The error bar indicates the observed spread of data for many samples using linear four-probe geometry. Note the log scale for $\sigma(P)/\sigma(0)$.

First we discuss the normal conductivity. It is tempting to attribute all the pressure dependence of $\sigma_{\parallel}$ to lattice-stiffening effects as occur in most other metals. However, such an interpretation is not consistent with (i) the striking similarity of pressure dependence of $\sigma_{\perp}$ and $\sigma_{\parallel}$, where the temperature dependence of $\sigma_{\perp}$ certainly does not show simple metallic behavior, and (ii) the magnitude of the pressure dependence which appears to be incompatible with a lattice effect assuming any reasonable elastic properties. From the pressure dependence of $\sigma_{\parallel}$ and assuming acoustic-phonon scattering, our data require that $\Delta\Theta_D/\Theta_D \approx 14\%$/kbar, while use of the Grüneisen formula $d(\ln\Theta_D)/dP = \beta V_0/C_v$ leads to $\Delta\Theta_D/\Theta_D = 1.2\%$/kbar. We have used the thermal expansion coefficient of trigonal Se[12] as an approximation to β of $(SN)_x$, and for the heat capacity C_v we use the high-temperature value of Harper *et al.*[13] for $(SN)_x$. Given the unreasonably large change in Debye frequency necessary to explain these data, we feel a band-structure change must play a significant role in the pressure dependence of normal conductivity.

We now discuss the pressure dependence of T_c. Assuming that the well-known McMillan[14] relation for T_c is obeyed in a superconductor as anisotropic as $(\mathrm{SN})_x$, two mechanisms can be visualized which would lead to an enhanced electron-phonon coupling constant $\lambda = N(0)\langle I^2\rangle / M\langle\omega^2\rangle$, and hence enhanced T_c, under pressure. Either the average phonon frequency $\langle\omega^2\rangle$ is anomalously reduced or $N(0)\langle I^2\rangle$ increases, where $N(0)$ is the density of states at the Fermi level and $\langle I^2\rangle$ is the usual Fermi surface average of the electron-phonon matrix element.

Although $(\mathrm{SN})_x$ is an *sp* metal, the parallel bandwidth obtained from optical data[15] and from band-structure calculations[15] is about 2–3 eV, which is more comparable with *d*-band metals. In perpendicular directions bandwidths are more like 0.5 to 1 eV. Thus a tight-binding approximation should be valid, for which[16] $N(0)\langle I^2\rangle \propto t^{-1}t^2 \propto t$. Both the normal conductivity ($\sigma_{\parallel}$ and $\sigma_{\perp}$) and our H_{c2} data discussed above suggest that t increases with pressure. Assuming no lattice contribution, we expect λ and hence T_c to increase with pressure. A recent pseudopotential calculation[17] on $(\mathrm{SN})_x$ indicates that $N(0) \propto t^{-1}$ decreases significantly under pressure, in agreement with our experimental results.

Now, what about the phonons? In other *sp* metals $\langle\omega^2\rangle$ usually dominates and, because pressure stiffens the lattice, T_c decreases. However, the chain structure of $(\mathrm{SN})_x$ is similar to the structures of trigonal selenium and tellurium. In these elements hydrostatic pressure results in an increase in the lattice parameter along the c axis (chain axis).[18] These anomalies in the elastic properties result in certain phonon modes softening under hydrostatic pressure.[19] The Raman and infrared spectra of $(\mathrm{SN})_x$[20] and the high-temperature specific heat[13] show behavior very similar to selenium. Thus it is possible that pressure will soften some phonon modes in $(\mathrm{SN})_x$. If these modes contribute to the electron-phonon coupling then the total pressure effect on $\langle\omega^2\rangle$ might be very small. It is possible that $\langle\omega^2\rangle$ could even decrease because of the contribution of these soft modes, but the increase in the room temperature σ makes this possibility seem unlikely.

In summary, we find that the increase of T_c and $\sigma(295^\circ\mathrm{K})$ with pressure up to 9 kbar are most consistently explained by a pressure-induced band-structure change. The exact nature of the change is not presently known; however, a calculation of the Fermi surface (with and without pressure) now in progress in our laboratory should help clarify the situation. Band structure changes have also been shown to be important in increasing T_c in transition-metal compounds.[16] We note that in this discussion we have accounted for the quasi-one-dimensional nature of $(\mathrm{SN})_x$ only by considering the anisotropy of the band structure and phonon spectrum. For example, we have assumed that the Coulomb potential (μ^*) is insensitive to pressure (as has been found in three-dimensional superconductors). However, as shown by Davis,[21] the effective Thomas-Fermi screening length, which determines both λ and μ^*, is strongly dependent upon the interchain separation in quasi-one-dimensional materials. This is an additional factor which must be taken into account in considering the pressure dependence of both σ and T_c. Clearly, much more experimental and theoretical work will be necessary to explain completely the unusual properties of $(\mathrm{SN})_x$ under pressure.

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Line Shape of the Magnetic Excitations in Substitutionally Disordered Antiferromagnets

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The neutron scattering from the magnetic excitations in the substitutionally disordered antiferromagnet, $Mn_{0.68}Zn_{0.32}F_2$, has been measured. The results show structure in the line shape which is similar to that predicted by some of the calculations based on the coherent-potential approximation and to that obtained in recent computer simulations.

The magnetic excitations in dilute antiferromagnets are ideal systems with which to test the predictions of theories for the excitations in disordered systems, because they may be studied in detail with neutron inelastic scattering techniques. The coherent-potential approximation (CPA) has been applied to these systems in several different ways. In the approach adopted by Buyers, Pepper, and Elliott,[1] each magnetic ion is treated as having an Ising energy determined by the number of neighboring magnetic ions, and the single-site CPA is used to evaluate the scattering of the excitations from these different energy levels. The line shape of the neutron scattering is then calculated and has considerable structure corresponding to these different possible single-ion energies. Similar structure has also been found in computer simulations of these systems.[2] In another approach[3,4] each magnetic ion is treated equivalently and the calculated line shape is smooth. Earlier experiments on these systems[5-8] have had insufficient experimental resolution to observe the fine structure and hence have been unable to distinguish clearly between these two theoretical predictions. In this Letter, we report on measurements with considerably improved experimental resolution which has enabled us to observe fine structure in the line