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<sup>1</sup>T. Appelquist and H. D. Politzer, Phys. Rev. Lett. **34**, 43 (1975); A. De Rújula and S. L. Glashow, Phys. Rev. Lett. **34**, 46 (1975).

<sup>2</sup>T. Appelquist *et al.*, Phys. Rev. Lett. **34**, 365 (1975); E. Eichten *et al.*, Phys. Rev. Lett. **34**, 369 (1975); J. Borenstein and R. Shankar, Phys. Rev. Lett. **34**, 619 (1975).

<sup>3</sup>G. Feinberg and J. Sucher, Phys. Rev. Lett. **26**, 681 (1971); referred to as FS.

<sup>4</sup>If the terms in  $U_{\text{eff}}$  are of the same order as  $X(r)$ ,

which would happen for axial-vector exchange, the overlap of  $|2S\rangle$  and  $|1S\rangle$  should not be treated by perturbation methods and may be of order 1. This would change the  $M1$  rates drastically. A term in  $V$  which is an odd Dirac operator on "1" and even on "2" (we know of no plausible model for this) would contribute a term  $\sim \langle \Phi_j | \times [\eta_1 \vec{\alpha}_1 \cdot \vec{\epsilon}, V] \Phi_i \rangle / (m_1 + m_2)$  to  $\mathfrak{M}_{\text{pair}}$  and lead to much larger decay rates.

<sup>5</sup>H. Schnitzer, "Hyperfine splitting of ground-state charmonium," Phys. Rev. D (to be published).

<sup>6</sup>By fitting  $\Gamma_e = 2.2$  keV of  $\psi(3.7)$  instead, we get  $m = 1.37$  GeV,  $b = 2.60$  GeV<sup>-1</sup>.

<sup>7</sup>B. Wiik, unpublished.

## Optical Properties of Polymeric Sulfur Nitride, (SN)<sub>x</sub> †

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We report polarized reflectivity measurements on crystalline (SN)<sub>x</sub> in the range of 0.25–6.0 eV. Our analysis of the data gives  $\hbar\omega_p = 4.6$  eV and  $m^* = 2m_e$ , values considerably different from those previously reported by other workers. The data also suggest that (SN)<sub>x</sub> has sufficient electronic dimensionality to suppress a Peierls distortion.

Recently Bright *et al.*<sup>1</sup> reported optical reflectivity data on films of the metallic polymer, polymeric sulfur nitride, (SN)<sub>x</sub>. From a Drude analysis of their data, they found an effective mass  $m^*$  equal to  $5.2m_e$  which implied a conduction bandwidth of only a few tenths of an eV. In this Comment, we present polarized reflectivity results obtained on single crystals of (SN)<sub>x</sub> over the range 0.25–6.0 eV. The analysis of our data suggests that the reduced effective mass is closer to  $2m_e$  with an associated one-dimensional (1D) bandwidth of 2.5 eV. This result is in much better agreement with band-structure calculations<sup>2</sup> and specific-heat data.<sup>3</sup> We show that our differences from the conclusions of Bright *et al.* essentially arise from their neglect of higher-energy interband transitions and an incomplete Drude analysis of their data. Similar conclusions have been reached subsequently by Pintschovius *et al.*<sup>4</sup>

A variety of measurements<sup>1-6</sup> on (SN)<sub>x</sub> indicate this material to be a highly anisotropic, possibly quasi one-dimensional, metal. In addition, (SN)<sub>x</sub> becomes superconducting at  $\sim 0.3^\circ\text{K}$ .<sup>7</sup> Since most other quasi-1D metals undergo a metal-insulator transition before reaching the superconducting state, it is important to understand why such a transition does not occur in (SN)<sub>x</sub>. The polarized optical data we present here help give insight into this question.

Our procedures for preparing (SN)<sub>x</sub> are de-

scribed in detail elsewhere.<sup>8</sup> Small, well-faceted, golden-colored crystals are usually obtained. Chemical analysis of the crystals yielded S, 69.62%; N, 30.63% (calculated S, 69.59%; N, 30.41%).<sup>8</sup> These values typify samples used in our previously reported work.<sup>3,7</sup> Beyond purity levels measurable by the usual analytical techniques, we feel the best available indication of purity to be the ratio of room-temperature to helium-temperature resistivity. Our average sample yielded  $R_{300}/R_{4.2} \approx 100$  with no observable resistance minimum at any temperature.<sup>8</sup> To our knowledge, these data represent the best conductivity results reported to date.

Our optical measurements were taken on a large crystal of face dimensions  $2.7 \times 1.3$  mm<sup>2</sup> with the long direction collinear with the monoclinic  $b$  axis. X-ray investigations of the face from which optical data were taken revealed strong  $(\bar{1}02)$  reflections with much weaker and broader  $(002)$  lines. No other reflections were observed. We conclude that our sample face contains primarily the  $(\bar{1}02)$  plane with some small amount of  $(100)$  twinning. The sulfur-sulfur nearest-neighbor direction, representing the greatest probable interchain interaction, lies coplanar with  $(\bar{1}02)$  and makes an angle of  $\sim 18^\circ$  with the  $E$  vector of near-normally incident light polarized perpendicular to the  $b$  axis.<sup>9</sup> Thus the  $E \perp b$  spectrum will sample a large portion of possible interchain interactions. Finally, the sur-

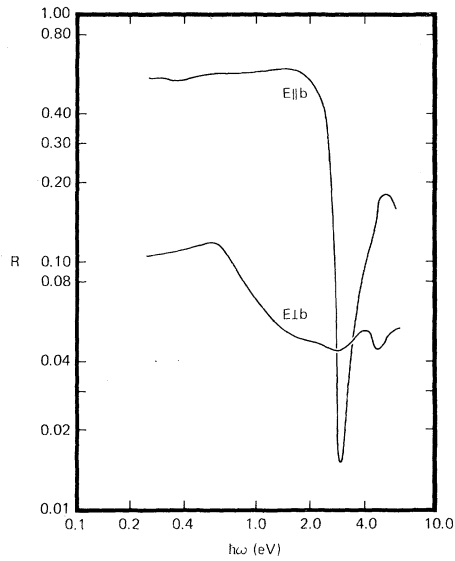


FIG. 1. Parallel ( $E \parallel b$ ) and perpendicular ( $E \perp b$ ) polarized reflectivity of crystalline  $(\text{SN})_x$  at room temperature.

face topology was sufficiently flat to permit specular, absolute, polarized reflectivity measurements to be made without the necessity of cleaving or polishing the sample.

Figure 1 summarizes our data. For  $E \parallel b$  polarization, we observe a steep, plasmlike reflectance edge, typical of metallic behavior, terminating at roughly 3 eV. In addition, relatively strong structure is observed near 5 eV. The spectrum for  $E \perp b$  demonstrates a much weaker rise toward the infrared, suggestive of low conductivity arising from intense scattering or trapping. Certainly our optical results confirm the view of  $(\text{SN})_x$  as at least a highly anisotropic metal. Note, however, the saturation of the  $E \parallel b$  response at a level near 60% in the region  $\hbar\omega < 1.5$  eV. This behavior may be due to increased non-specular reflection from the sample surface, or the presence of small-gap interband transitions embedded in an otherwise metallic optical response. On the basis of preliminary 3D OPW band-structure calculations,<sup>3</sup> there is evidence to support the latter interpretation.

At roughly 4.0 eV, structure consisting of a peak and shoulder appears in the  $E \perp b$  and  $E \parallel b$  spectra, respectively, with an additional peak occurring near 5.4 eV in the parallel data alone. It would be premature to attempt assignment of this structure until refinement of our OPW calculations. Its present importance lies in establishing the proximity of strong interband transitions

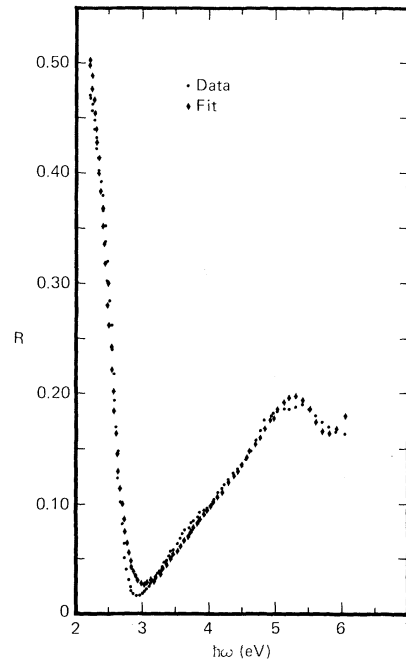


FIG. 2. Line-shape analysis of  $E \parallel b$  data near the reflectance edge. Crosses indicate a typical least-squares fit of one Drude plus two Lorentzian functions. The following parameters were obtained: (1) Drude:  $\epsilon_\infty = 1$  (fixed),  $\hbar\omega_p = 5.5$  eV,  $\tau/h = 1.8$  eV<sup>-1</sup>; (2) Lorentzians:  $\hbar\omega_{01} = 5.4$  eV,  $\hbar\omega_{p1} = 3.8$  eV,  $\tau_1/h = 1.1$  eV<sup>-1</sup>,  $\hbar\omega_{02} = 7.4$  eV,  $\hbar\omega_{p2} = 11.5$  eV,  $\tau_2/h = 5.5$  eV<sup>-1</sup>. The root  $\chi^2$ ,  $[\chi^2]^{1/2}$ , was 0.031. We do not attach any particular physical significance to the Lorentzian lines.

near the reflectance minimum which are polarized along the  $b$  axis. The parallel data were subsequently analyzed by a Drude-Lorentz fit of the following form for the complex dielectric constant:

$$\epsilon = \epsilon^f + \epsilon^b,$$

where

$$\epsilon^f = -\omega_p^2 / (\omega^2 - i\omega/\tau),$$

and

$$\epsilon^b = 1 + \sum_n \omega_{pn}^2 / [(\omega_{0n}^2 - \omega^2) + i\omega/\tau_n].$$

Here  $\epsilon^f$  and  $\epsilon^b$  denote intraband and interband terms, respectively, with  $\epsilon^f$  containing the Drude parameters  $\omega_p$  and  $\tau$ . The results of a fit using two Lorentzian lines for  $\epsilon^b$  is shown in Fig. 2. Of particular significance is the position of the reflectance minimum relative to the value of  $\hbar\omega_p = 5.5$  eV obtained for the unscreened plasma energy. It is well known that the reflectivity minimum occurs near an energy  $\hbar[\omega_p^2/\epsilon_1^b(\omega_{\min})]^{1/2}$ ,

where we have  $\epsilon_1^b(2.8 \text{ eV}) = 3.6$  for  $(\text{SN})_x$ . Different numbers of Lorentzian lines were tried. By and large, all fits were uniformly poor as determined by their root- $\chi^2$  values. As many as five Lorentzians were applied spread both above and below the reflectance minimum; however, we never bettered the representative example given in Fig. 2. It is not entirely clear why better fits could not be obtained; perhaps inherent energy dependences in the line parameters must be taken into account. Nevertheless, we feel that the sum total of our analyses justifies bracketing the plasma energy and Drude lifetime within boundaries of  $4.6 \pm 1 \text{ eV}$  for  $\hbar\omega_p$  and  $1.6 \pm 0.3 \text{ eV}^{-1}$  [ $(1.0 \pm 0.25) \times 10^{-15} \text{ sec}$ ] for  $\tau/\hbar$ .

Our parameters contrast markedly with those of Bright *et al.*<sup>1</sup> who obtained  $\epsilon_{\text{core}} = 1.46$  [our  $\epsilon_1^b(0)$ ],  $\hbar\omega_p = 2.8 \text{ eV}$ , and  $\tau = 1.9 \times 10^{-15} \text{ sec}$  based on a single Drude line-shape analysis over a limited range of data. They state that attempts to fit their data to energies above 2.8 eV led to "an unreasonably high value for  $\epsilon_{\text{core}}$  ( $> 5$ )." However, high-background dielectric constants in metals are actually quite common and arise from strong interband transitions near the unscreened plasma energy.<sup>10</sup> Interestingly, upon reanalyzing the data presented in Fig. 3 of Ref. 1a for the region 1.7–2.8 eV, we were able to find a more optimum fit than their published values. The results are shown in our Fig. 3 where we obtain the Drude parameters  $\epsilon_{\text{core}} = 4.1$ ,  $\hbar\omega_p = 5.1 \text{ eV}$ , and  $\tau = 1.2 \times 10^{-15} \text{ sec}$ , giving a fourfold improvement in the root  $\chi^2$  over the published fit. Thus, when analyzed more thoroughly, the results of Bright *et al.*

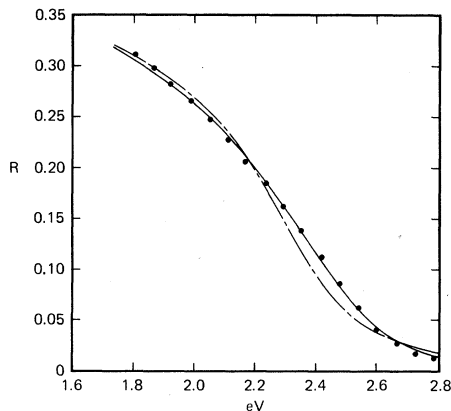


FIG. 3. Reanalysis of the Penn film data (Ref. 1). The solid line indicates the best Drude fit, with  $[\chi^2]^{1/2} = 0.006$ , as determined by our least-squares calculations. The broken line is the published Penn fit, with  $[\chi^2]^{1/2} = 0.025$ .

are in near agreement with our  $E \parallel b$  data.

From  $\omega_p$  one can determine  $n/m^*$ , where  $n$  is the carrier concentration and  $m^*$  the effective mass. Preliminary band-structure calculations indicate that separate hole and electron pockets may exist within the Brillouin zone, in which case  $n/m^*$  will reflect the effects of electron-hole concentrations and effective masses (see Rudge and Grant<sup>2</sup> and Friesen *et al.*<sup>2</sup>). For  $\hbar\omega_p = 4.6 \text{ eV}$  and  $n = 3.05 \times 10^{22} \text{ carriers/cm}^3$ , we find  $m^* \approx 2$ , implying roughly 2.5 eV for a crude 1D tight-binding estimate of the bandwidth. This degree of band dispersion is in much better agreement with experiment and theory than that suggested by the analysis in Ref. 1a.

Turning now to the  $E \perp b$  data, we direct attention to the slight rise in reflectivity from  $\sim 5\%$  in the visible to  $\sim 13\%$  in the infrared. Similar data were also reported in Ref. 1b for oriented  $(\text{SN})_x$  films and polished crystals and were interpreted as evidence of interchain interaction. Within the framework of one-electron band theory, any finite amount of electronic interchain coupling must result in some level of metallic conductivity. However, if the interchain bandwidth is narrow, the predominant physical mechanism limiting conduction is certain to be carrier scattering and trapping effects rather than electronic dispersion. The upward tendency of the perpendicular reflectivity does suggest some interchain overlap but with strong damping of carrier motion in this direction. Nonetheless, this small amount of interaction may provide the clue to the low-temperature stability of the conducting state in  $(\text{SN})_x$  in that enough incommensurability is created among the various Fermi vectors and sufficient dimensionality introduced in the Fermi surfaces to suppress a Peierls distortion. Further supportive evidence of significant interchain interaction comes from our observation of superconductivity perpendicular to the  $b$  axis at the same critical temperature as in the parallel direction.

In summary, we have shown that single-crystal polarized reflectivity measurements on  $(\text{SN})_x$  reveal the presence of interband transitions which screen the free-electron plasma energy resulting in a smaller effective mass than previously reported. In addition, an in-depth analysis of the film data of Bright *et al.* supports our crystal findings.

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sions with A. A. Bright and M. J. Cohen concerning their film data, and thank the latter for pointing out a typographical error in the manuscript of this Comment.

†First reported in G. B. Street, P. M. Grant, and R. L. Greene, *Bull. Am. Phys. Soc.* **20**, 360 (1975).

<sup>1a</sup>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>1b</sup>A. A. Bright, M. J. Cohen, A. F. Garito, A. J. Heeger, C. M. Mikulski, P. J. Russo, and A. G. MacDiarmid, *Appl. Phys. Lett.* **26**, 612 (1975).

<sup>2</sup>W. E. Rudge and P. M. Grant, *Bull. Am. Phys. Soc.* **20**, 359 (1975), and to be published; W. I. Friesen, A. J. Berlinsky, B. Bergersen, L. Weiler, and T. M. Rice, *Bull. Am. Phys. Soc.* **20**, 360 (1975), and to be published; H. Kamimura, A. J. Grant, F. Levy, A. D. Yoffe, and G. D. Pitt, *Solid State Commun.* **17**, 49 (1975); V. T. Rajan and L. M. Falicov, to be published; D. E. Parry and J. M. Thomas, *J. Phys. C: Solid State Phys.* **8**, L45 (1975); A. Zunger, to be published; M. Kertesz, J. Koller, and A. Azman, to be published.

<sup>3</sup>R. L. Greene, P. M. Grant, and G. B. Street, *Phys. Rev. Lett.* **34**, 89 (1975).

<sup>4</sup>L. Pintschovius, H. P. Gesserich, and W. Möller, to be published.

<sup>5</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>6</sup>H. J. Stolz, A. Otto, M. Cardona, and L. Pintschovius, to be published.

<sup>7</sup>R. L. Greene, G. B. Street, and L. J. Suter, *Phys. Rev. Lett.* **34**, 577 (1975).

<sup>8</sup>G. B. Street, H. Arnal, W. D. Gill, P. M. Grant, and R. L. Greene, *Mater. Res. Bull.* **10**, 877 (1975).

<sup>9</sup>M. Boudeulle, *Cryst. Struct. Commun.* **4**, 9 (1975).

<sup>10</sup>J. A. Benda, R. E. Howard, and W. A. Phillips, *J. Phys. Chem. Solids* **35**, 937 (1974). More classic examples occur in Ag [H. Ehrenreich and H. R. Philipp, *Phys. Rev.* **128**, 1622 (1962)], and in  $\text{ReO}_3$  [J. Feinleib, W. J. Scouler, and A. Ferretti, *Phys. Rev.* **165**, 765 (1968)]. Occasionally the reflectivity minimum occurs at energies higher than the unscreened plasma energy as a result of very strong low-energy interband transitions as in Al [H. Ehrenreich, H. R. Philipp, and B. Segall, *Phys. Rev.* **132**, 1918 (1963)]. Although the preliminary OPW calculations suggest the possibility of small-gap interband transitions in  $(\text{SN})_x$ , we have no evidence, theoretical or experimental, that they would be strong enough to produce an effect similar to what occurs in Al.

## Energy-Level Parities at $L$ in PbTe

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The implications of the new parity labeling of the band states at  $L$  by Glosser, Kinoshita, and Rennex are discussed and shown to lead to properties which are difficult to reconcile with theoretical calculations and some experiments.

Glosser, Kinoshita, and Rennex<sup>1</sup> (GKR) have recently suggested that the accepted parities at the  $L$  point of the Brillouin zone for PbTe are inconsistent with their measurements of band-population effects in electroreflectance spectra. This is of particular interest since the minimum gap in this narrow-gap semiconductor is at  $L$  and the ordering of the states in this region is intimately related to the physical properties of this material.

The reordering of the levels involves bands 3 to 8 at  $L$ . There are five valence bands in PbTe and the gap ( $\sim 0.2$  eV) appears between bands 5

and 6, i.e.,  $L(6) - L(5)$ . Most band-structure calculations on this material (and other Pb salts) yield positive parities for bands  $L(3)$  to  $L(5)$  and negative parities for bands  $L(6)$  to  $L(8)$ . These include current-pseudopotential,<sup>2,3</sup> orthogonal-plane-wave,<sup>4</sup> augmented-plane-wave,<sup>5</sup> and Green's-function<sup>6</sup> calculations. The reordering suggested by GKR is based on nonobservation of critical-point transitions at  $L$ , and the subsequent conclusion that this implies that bands  $L(5)$ ,  $L(7)$ , and  $L(8)$  have one parity while bands  $L(3)$ ,  $L(4)$ , and  $L(6)$  have the other. GKR suggest that the above assignment would result in several parity-