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One Dimensional Conductors
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Optical Properties of $(SN)_X$ Films. G. B. STREET, P. M. GRANT and R. L. GREENE, IBM San Jose.-- The reflection and transmission spectra of thin polycrystalline films of polysulphur nitride $(SN)_X$ have been recorded in the wavelength range 2000Å - 40μ. A reflectance edge of medium steepness is observed near 2.5eV which is possibly associated with metallic behavior. Structure in the infrared occurs at 10.1, 13.2, 15.0, 16.2 and 21.0μ which is due to vibrational or vibronic states. The metallic-like reflectance edge is analyzed in terms of a tight-binding model for various band parameters and the results compared to findings from specific heat data.

Submitted by

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several clusters in the same crystal. The results of the two methods will be compared with each other and to available experimental results.

[1]Boudeulle, Micheline, Ph.D. Thesis, "Contribution à l'étude crystallographique d'un composé moléculaire en chaine - Cas du polynitrure de soufre $(SN)_x$", L'universite Claude-Bernard de Lyon (1974)

CM 2 LCAO Band Structure for $(SN)_x$. W.I. FRIESEN, A.J. BERLINSKY, B. BERGERSEN, L. WEILER, University of British Columbia and T.M. RICE, Simon Fraser University--The band structure of the conducting polymer $(SN)_x$ has been calculated by a generalization of the extended Hückel method of Hoffman with use made of the crystal structure determination of Boudeulle[1]. The Fermi level is found to lie in a band made up of anti-bonding π-orbitals. Because of the presence of a screw axis there is a zone boundary degeneracy which gives rise to metallic behaviour. When interchain coupling is ignored the usual instabilities associated with one dimensional metals are expected. The role of interchain coupling in stabilizing the three dimensional structure is investigated.

1. M. Boudeulle, Thesis, University of Lyon 1974.

CM 3 Pressure Dependence of Conductivity in Polysulfur Nitride $(SN)_x$. W. D. GILL and G. B. STREET, IBM Research Laboratory, San Jose, Calif.--Crystals of $(SN)_x$ have been reported[1] to behave like a one-dimensional metal with room temperature conductivity along the fiber axis as high as 1730 $\Omega^{-1}cm^{-1}$. We report the effect of hydrostatic pressure on the 4-probe dc conductivity of $(SN)_x$ crystals over the temperature range from 4°K to 300°K. At high temperatures where the conductivity varies inversely with temperature[1] there is an initial very strong increase with pressure saturating at $\sigma(P)/\sigma(0) \simeq 6$ for $P \simeq 12$ kbar. The implications of the pressure dependence of conductivity on the electronic structure and on transport properties will be discussed.

[1]V. V. Walatka, Jr., M. M. Labes and J. H. Perlstein, Phys. Rev. Lett. 31, 1139 (1973).

CM 4 The Dimensionality of $(SN)_x$. MARSHALL J. COHEN, C. K. CHIANG, A. F. GARITO, A. J. HEEGER, A. G. MACDIARMID, and C. M. MIKULSKI, Univ. of Penna.--The thermopower and dc conductivity were measured as a function of temperature both parallel and perpendicular to the chain axis of $(SN)_x$. At room temperature, the parallel and perpendicular thermopowers are -1.5 and -3.5 $\mu V\text{-}K^{-1}$, respectively, while the parallel conductivity is approximately 2.5×10^3 $\Omega^{-1}\text{-}cm^{-1}$. The measured perpendicular conductivity is smaller and dominated by the polycrystalline nature of the samples in that direction. These data together with the polarized reflectance and low temperature specific heat data are used to discuss the dimensionality of the electrical properties of $(SN)_x$.

CM 5 Polarized Reflectance of $(SN)_x$. A. A. BRIGHT, M. J. COHEN, A. F. GARITO, A. J. HEEGER, A. G. MACDIARMID, and C. M. MIKULSKI, Univ. of Penna.--Polarized reflectance measurements have been made on single crystals and epitaxial films of polymeric sulfur nitride $(SN)_x$ from 500 cm^{-1} to 30,000 cm^{-1}. The spectra of the films and of the crystals agree well. The observed anisotropic reflectance is consistant with $(SN)_x$ being a highly anisotropic metal. For polarization parallel to the polymer axis, a Drude-like reflectivity is observed with a plasma edge at 22,000 cm^{-1} (2.85 eV), and a high reflectance throughout the infrared. The results for both parallel and perpendicular polarization will be discussed in relation to the electrical, thermal, and magnetic properties of this material.

CM 6 Optical Properties of $(SN)_x$ Films. G. B. STREET, P. M. GRANT and R. L. GREENE, IBM San Jose.--The reflection and transmission spectra of thin polycrystalline films of polysulphur nitride $(SN)_x$ have been recorded in the wavelength range 2000Å - 40μ. A reflectance edge of medium steepness is observed near 2.5eV which is possibly associated with metallic behavior. Structure in the infrared occurs at 10.1, 13.2, 15.0, 16.2 and 21.0μ which is due to vibrational or vibronic states. The metallic-like reflectance edge is analyzed in terms of a tight-binding model for various band parameters and the results compared to findings from specific heat data.

CM 7 Low Temperature Specific Heat of Polysulfur Nitride, $(SN)_x$.* J.M.E. HARPER, Stanford Univ. and P.M. GRANT, G.B. STREET, and R.L. GREENE, IBM Res. Lab., San Jose--Specific heat measurements of crystalline $(SN)_x$ have been made over the range 1.5°K to 55°K. A fit of the data below 3.2°K to the relation $C = \gamma T + \beta T^3$ yields $\gamma = 18 \pm 2 \times 10^{-6}$ j/gm-K^2, and $\beta = 8.8 \pm 0.4 \times 10^{-6}$ j/gm-K^4. The linear temperature term is interpreted as arising from an electron state density of 0.18 states/eV-spin-molecule. Above 3.2°K the lattice heat capacity departs dramatically from T^3 behavior. The region from 4°K to 25°K follows a $T^{5/2}$ dependence with a gradual transition to lower temperature dependences above 25°K. This result is consistent with the chain-like structure of $(SN)_x$ and suggests the interchain coupling is weak. No evidence of a discrete phase transition was found between 1.5 and 55°K.

*Research at Stanford sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant No. AFOSR-73-2435A.

CM 8 Conductivity of Polysulfur Nitride Below 4.2°K. R. L. GREENE and G. B. STREET, IBM San Jose, and L. J. SUTER*, Stanford University.--The d.c. conductivity (σ) of $(SN)_x$ has been measured between 0.07°K and 4.2°K. The conductivity remains metallic-like down to .07°K, i.e. no metal-insulator transition occurs as in other quasi one-dimensional conductors. The significance of this result for understanding the phase transition in other 1D conductors will be discussed.

*Present address: Lawrence Livermore Laboratory

CM 9 Anomalous Pressure Dependence of the Metal-Nonmetal Transition of NiS.* R. E. Jones Jr. and W. J. Keeler, Lakehead U., Thunder Bay, Ont.--Electrical resistivity measurements were used to determine the pressure dependence of the metal-nonmetal transition temperature, T_t, in hexagonal NiS to 14 kbar. Below 4 kbar, pressure suppresses the transition with $dT_t/dP = -8.4$ K/kbar for a powdered sample with $T_t = 266$ K at zero pressure. However, near 4.5 kbar a local increase in T_t is observed. Above 5 kbar T_t again decreases with pressure and the magnitude of the pressure derivative appears to be somewhat greater than at low pressures. This result is consistent with the neutron diffraction work of Smith and Sparks[1] who found that the a- and c-axis parameters show an anomalous increase for a small pressure interval near 5 kbar.

[1]F. A. Smith and J. T. Sparks, J. Appl. Phys. 40,1332 (1969).

*Supported by grants from the Defence Research Board and the National Research Council of Canada.

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Polarized Reflectance of Polysulfur Nitride, $(SN)_x$, in the Range 0.25 - 6.0 eV

Outline

According to a variety of measurements, polysulfur nitride exhibits physical properties characteristic of an anisotropic metal with a single strongly preferred direction of conduction - in other words, a quasi-one-dimensional metal.(1) Analysis of its crystal structure indicates a monoclinic unit cell consisting of four (SN) groups arranged in such a way as to form the basis of two counter-rotating polymeric strands.(2) Specific heat measurements have confirmed the intrinsic metallic nature of the conductivity of $(SN)_x$ and the existence of lattice anisotropy.(3) Recently, $(SN)_x$ was found to become superconducting at 0.25 °K, an unexpected result given the elements involved.(4) Because most other materials thought to behave as quasi-one-dimensional metals at high temperatures undergo a metal-insulator transition before reaching the superconducting state, it is vital to understand why this is not the case for $(SN)_x$,

~~We have performed polarized reflectance measurements on single crystals of $(SN)_x$~~

and, in particular, the role of interchain coupling (or lack thereof) in determining a given ground state. (over)

We have performed the first polarized reflectance measurements on single crystals of $(SN)_x$ in order to help answer some of these questions. The single crystals were grown by techniques discussed elsewhere with purity levels consistent with previously reported results.(5)

{ Orientation of surface and further description }

965-IBM-10

* This point is especially pertinent to any discussion of the possibility of fabricating a Little-type excitonic superconductor utilizing an isolated $(SN)_x$ chain as a conducting spine.

The sample reported on here was a large single crystal of face dimensions ~~~~~ mm. The face itself was found to contain the $(10\bar{2})$ crystallographic so that both polarization directions ($E \parallel b$ and $E \perp b$) were coplanar with the sulfur - sulfur nearest neighbor interchain distance. For $E \perp b$, the angle with this distance was ~~~. The morphological perfection of the surface was sufficient to allow specular, near normal incidence, polarized reflectivity measurements to be made.

* ~~On the basis of a preliminary OPW band structure calculation,~~

note, however, the saturation of the E⊥b reflectivity at a level around 60% as we moves from the reflectance edge into the infrared. This behavior may be due to increased non-specular scattering from the sample surface, or the presence of a small gap interband transition embedded in an otherwise metallic optical response. On the basis of preliminary 3-D OPW band structure calculations, (2) there is evidence to support the latter explanation based on the existence of at least two interband transitions in the neighborhood of 0.5 eV.

Turning to the E⊥b data, we note as before the slight rise in reflectivity from the visible to the IR culminating in a value of roughly 15% at 0.2 eV. Within the framework of one-electron band theory, any finite amount of interchain coupling is bound to result in some level of metallic conductivity. However, the predominant physical mechanism determining the conductivity is certain to be carrier scattering and lifetime effects rather than electronic dispersion when this coupling is weak. The preliminary OPW calculation indicate the presence of overlapping bands resulting in hole-electron pockets occupying a relatively small portion of the Brillouin zone in the high conductivity direction. The extent of these pockets in the transverse direction is as yet unknown and

The perpendicular reflectivity behavior of the ~~that~~ does suggest ~~is very suggestive~~ that some interchain overlap ~~occurs~~ but that electronic motion is strongly damped in this direction. Nonetheless this small amount of interaction may provide the clue to the low temperature stability of the conducting state in (SN)$_x$ in that enough

dimensionality occurs in the Fermi surfaces to preclude the onset of a Peierls distortion. Further supportive evidence of finite interchain interaction arises from the fact that superconductivity also occurs perpendicular to the b axis at the same critical temperature as in the parallel direction.

At roughly 4.0 eV, a peak and a shoulder appear in the E⊥b and E∥b data, respectively, with an additional peak occurring near 5.4 eV in the parallel spectrum 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 near the reflectance minimum which is polarized along the b-axis. This fact could not be determined from earlier film data and has direct consequences for the Drude analysis to follow.

In several metals, notably As and ReO_3, this has meant that the free electron plasma energy turned out to be much greater than the energy at the reflectance minimums. We attempted to account for the effect of interband transition by adding one or more Lorentzian lines to the usual Drude lineshape. By and large, the fits were uniformly poor as determined by their root-chi-square. However employing Lorentzians invariably gave better results than using a Drude model alone. In Fig. 2 we have shown a representative fit. It is not entirely clear why better fits could not be obtained; perhaps inherent ~~frequ~~ energy dependencies in the fitting parameters themselves must be taken into account. Nevertheless, we feel able to bracket the plasma frequency and Drude lifetime within boundaries of 4.5 ± 1.0 eV for $\hbar\omega_p$ and 1.3 ± 0.2 for $\tau/\hbar$, respectively. Note that the value for the plasma energy is considerably greater than that found from recently published Kikuchi data where the effect of interband transition were not taken into account.

Figure 1 summarizes our ~~measurements~~ data. For light polarized with E⊥b, we observe a steep reflectance edge, typical of metallic behavior, terminating at roughly 3.0 eV. In addition, relatively strong structure is observed near 5.0 eV which will assume central importance in our later discussion. On the other hand, the spectrum for E∥b indicates a much weaker rise toward the infrared indicative of low conductivity arising from strong scattering. Certainly, the optical results underline the view of $(SN)_x$ as a highly anisotropic metal.

{ Put in preliminary assignments (2a) }*

~~The results of our optical constant analysis is given in Fig. 2.~~

The results of our optical constant analysis, in terms of Drude-Lorentz oscillators, for energies near the reflectivity edge and higher are shown in Fig. 2. Of particular importance in the E⊥b spectrum is the position of the reflectance minimum relative to the value of the plasma energy. It is readily apparent that the energy of the minimum is severely depressed by the presence of strong interband transitions in the range 3-5 eV and above. From values of the plasma energy (Figure 2 Inset (a)) one can determine n/m^* from the relation $\omega_p^2 = 4\pi e^2 (n/m^*)$. Beyond this ratio one cannot proceed without further information. In particular, one must consider the possibility of the existence of separate hole and electron pockets as discussed above.

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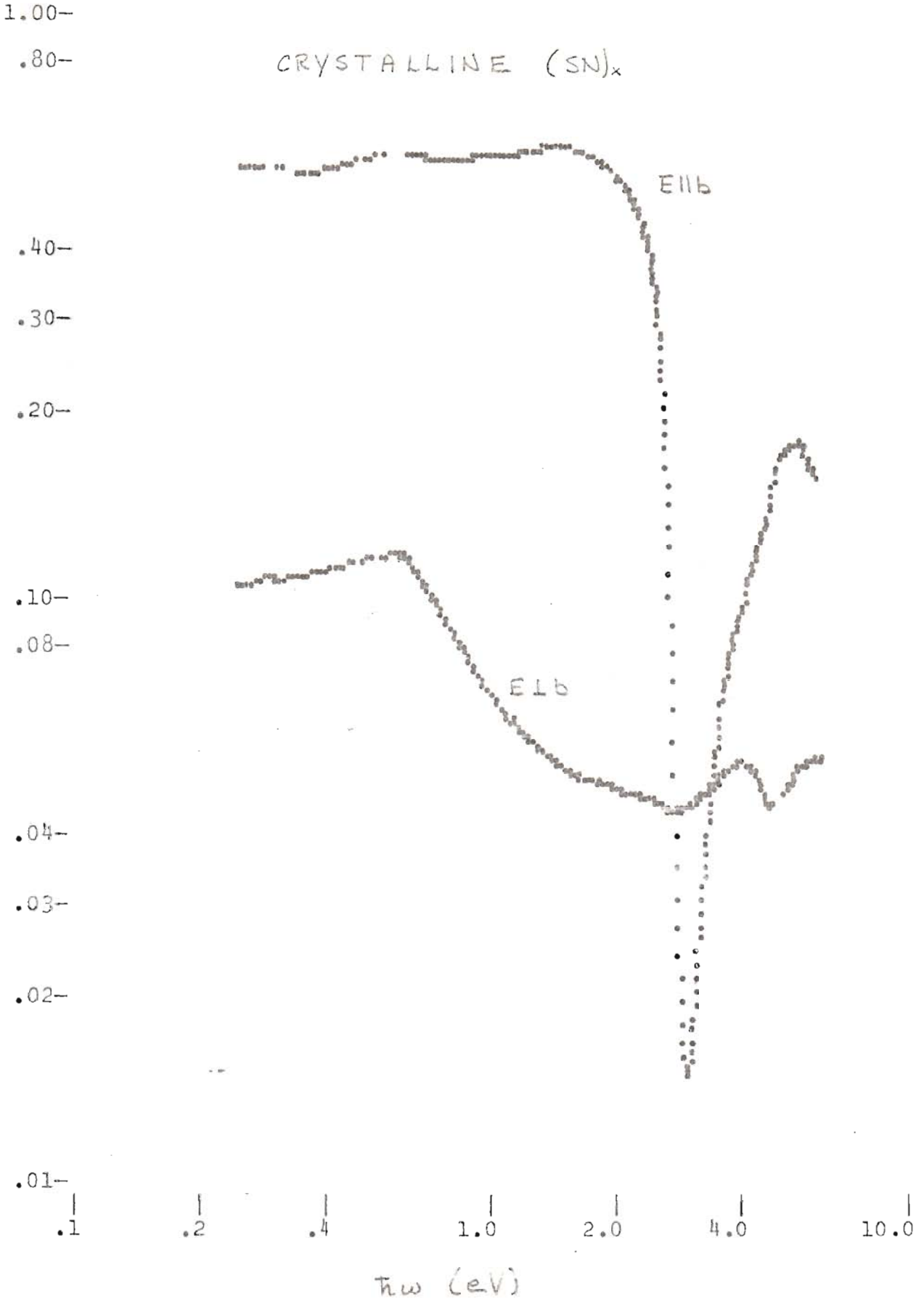
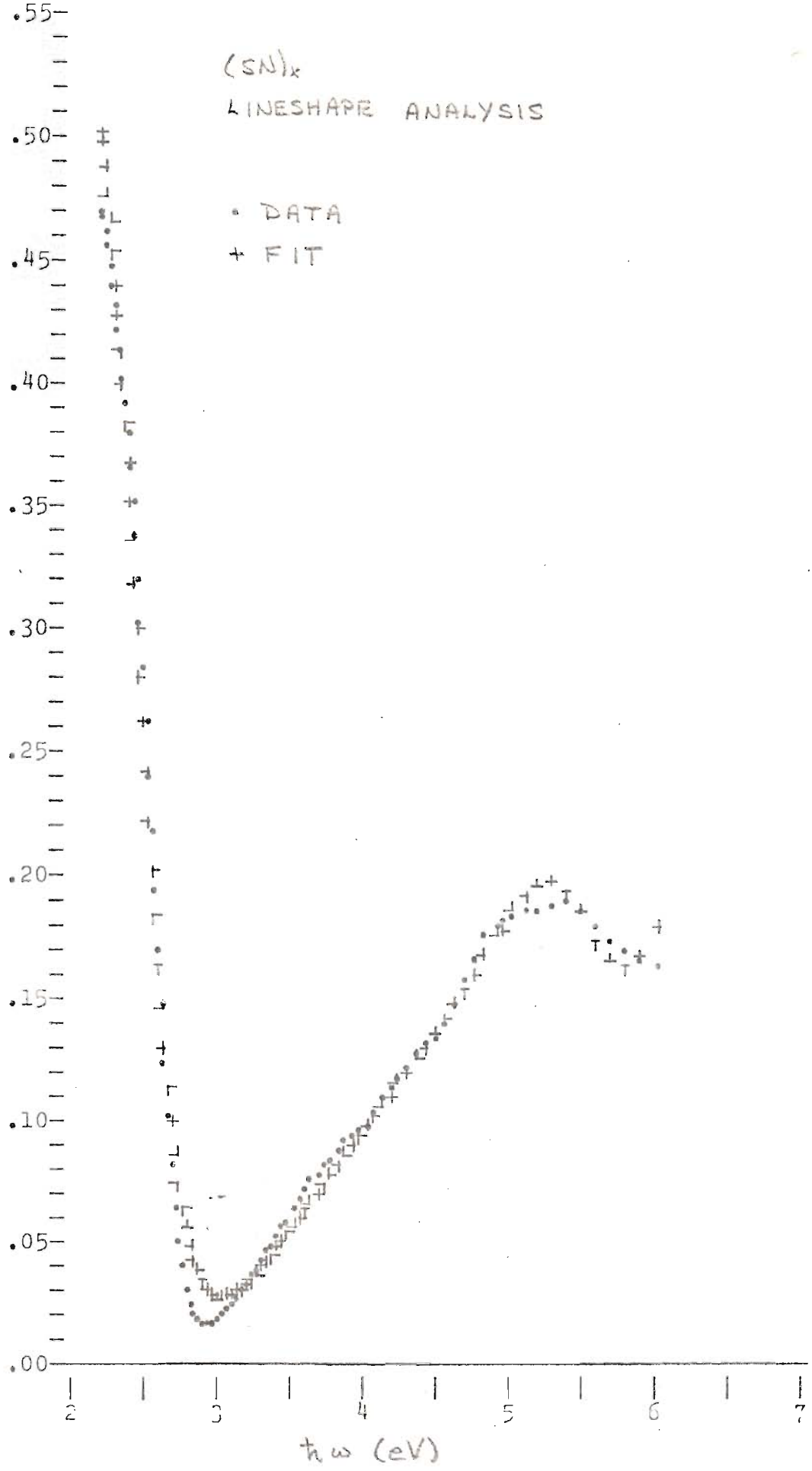
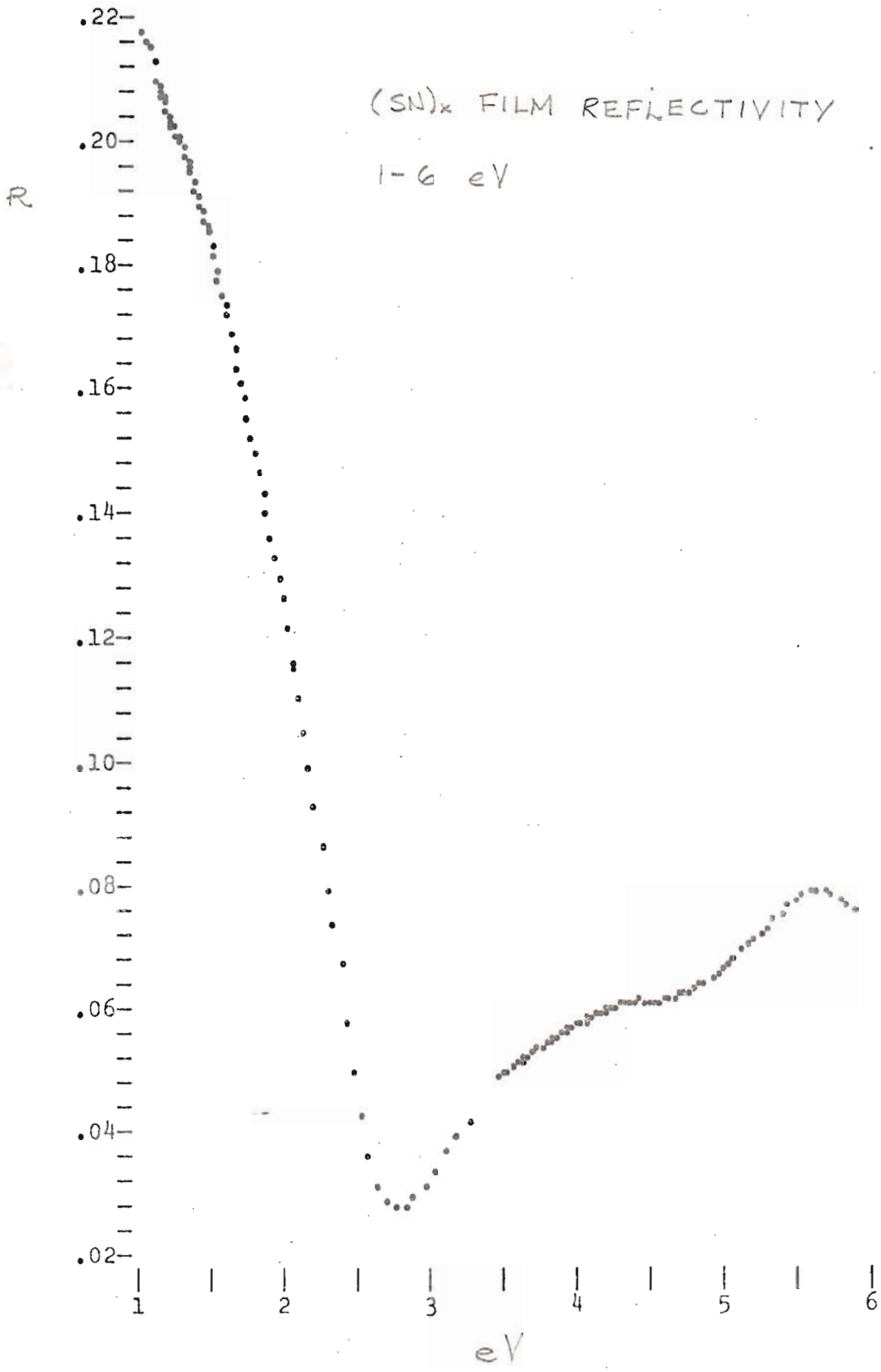
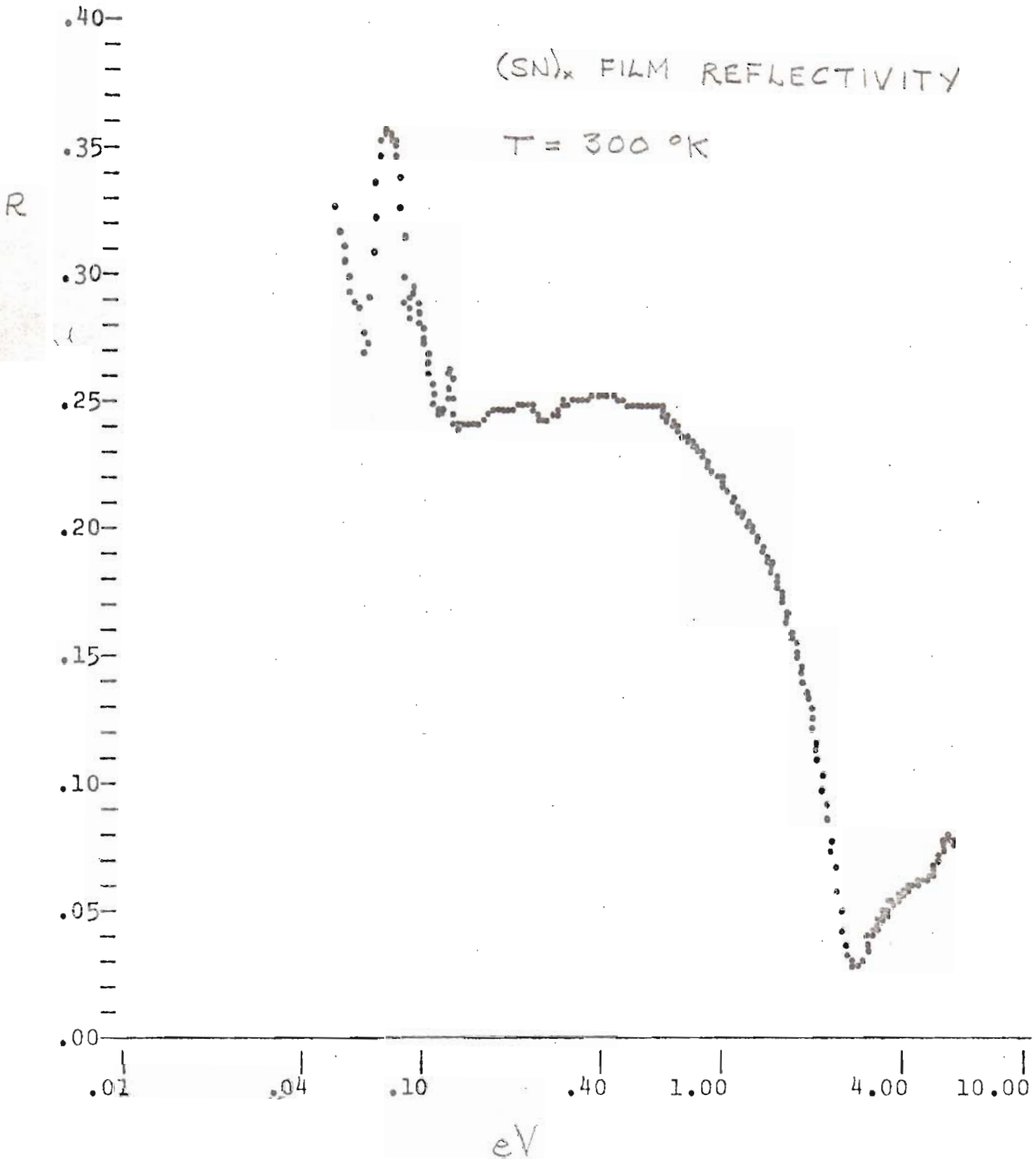
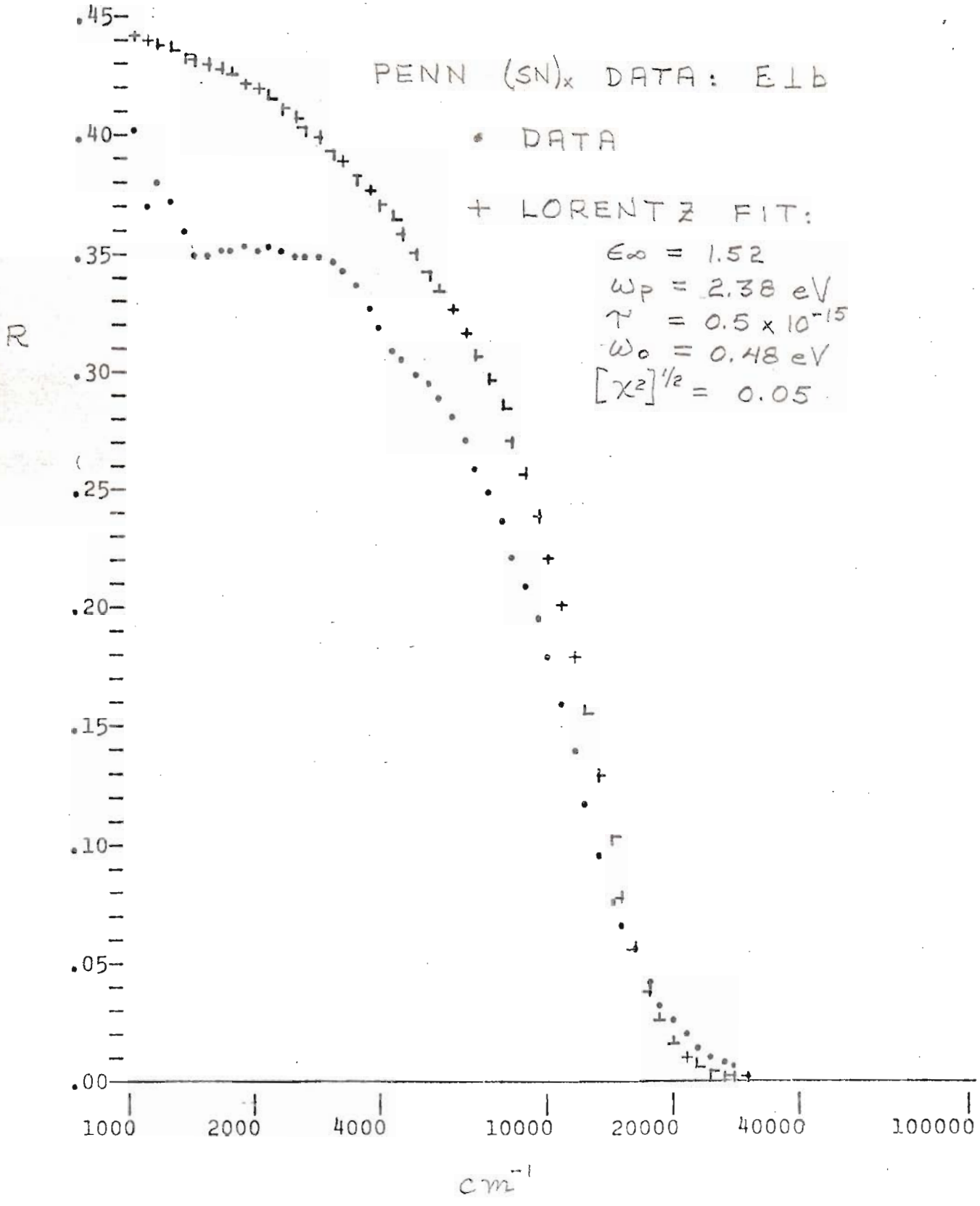
In this case, one must consider the plasma energy as given by $\omega_p^2 = 4\pi e^2 n_c (m_e^* + m_h^*)/m_e^* m_h^*$. In the absence of detailed knowledge concerning the respective electron and hole effective masses, we are better off analyzing the plasma frequency in terms of the effective number of carriers given by $\omega_p^2 = 4\pi e^2 n_{eff} N/M_0$ where N is the number of SN molecules per unit cell, thus gaining an idea of the number of electrons contributing to the metallic optical properties.

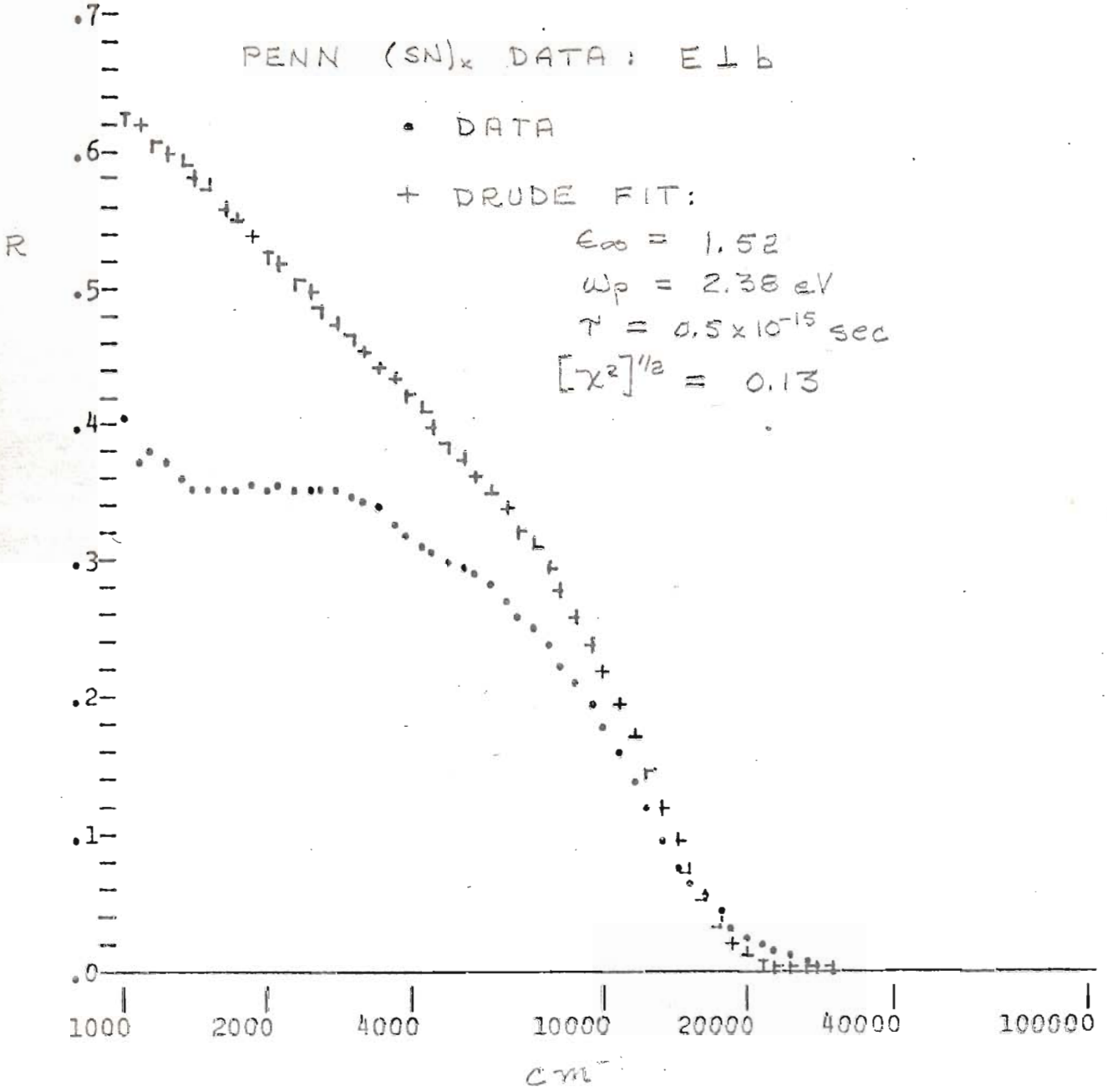

CRYSTALLINE (SN)x
E||b
E⊥b
R
1.00
.80
.40
.30
.20
.10
.08
.04
.03
.02
.01
.1
.2
.4
1.0
2.0
4.0
10.0
ħω (eV)

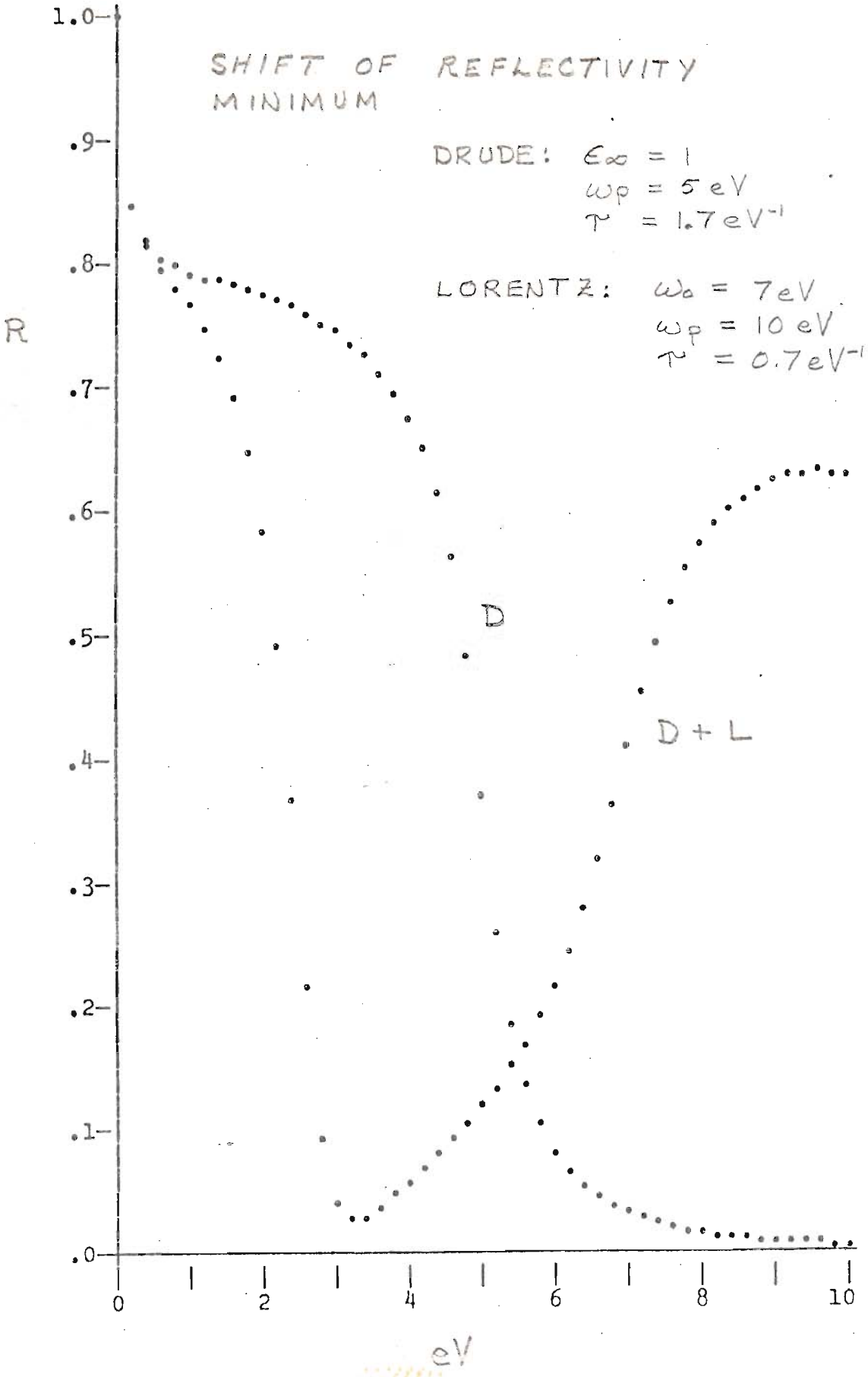

(SN)x
LINESHAPE ANALYSIS
• DATA
+ FIT
R
.55
.50
.45
.40
.35
.30
.25
.20
.15
.10
.05
.00
2
3
4
5
6
7
ħω (eV)

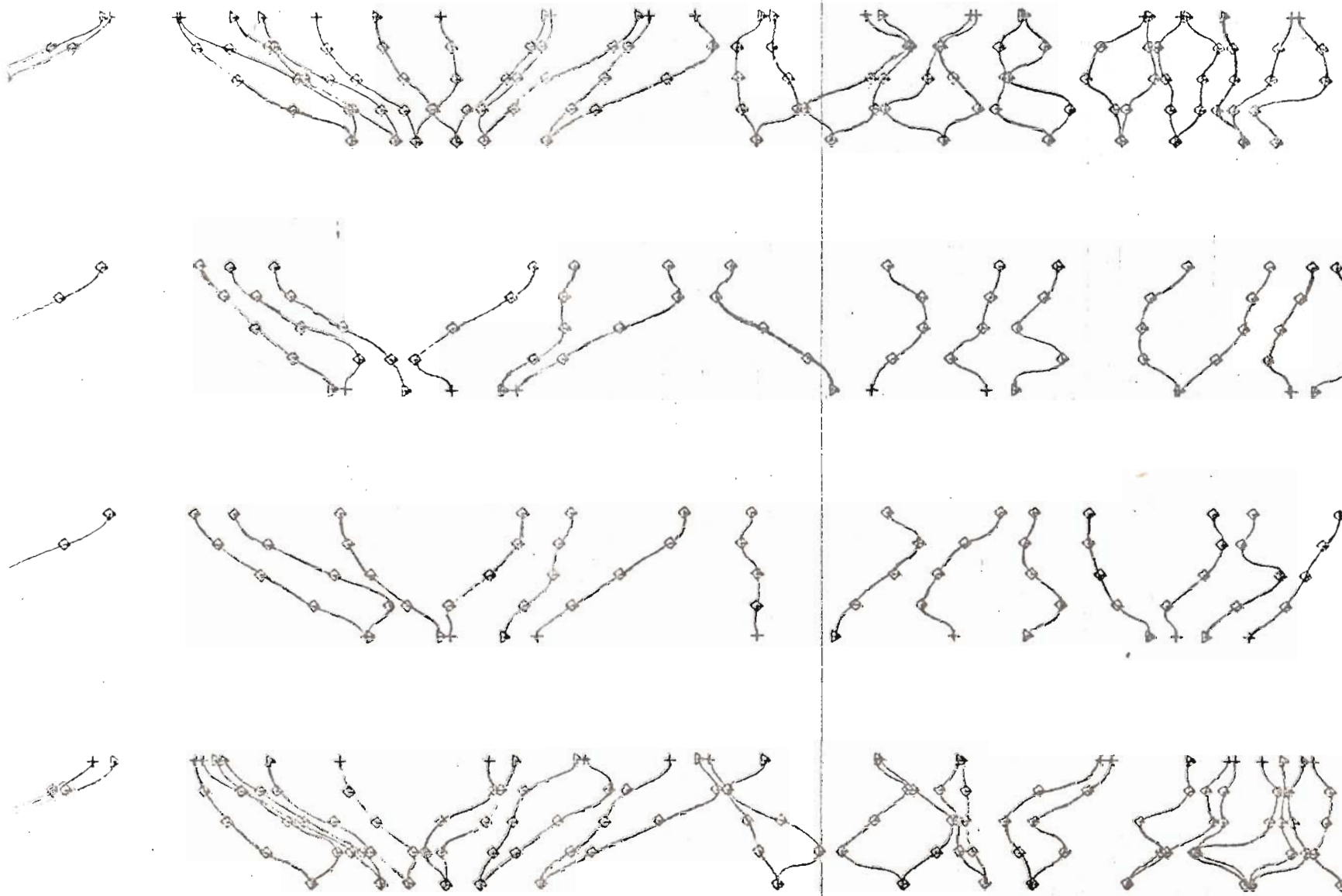

(SN)x FILM REFLECTIVITY
1-6 eV
R
.22
.20
.18
.16
.14
.12
.10
.08
.06
.04
.02
1
2
3
4
5
6
eV


(SN)x FILM REFLECTIVITY
T = 300 °K
R
.40
.35
.30
.25
.20
.15
.10
.05
.00
.01
.04
.10
.40
1.00
4.00
10.00
eV


PENN (SN)x DATA: E⊥b
• DATA
+ LORENTZ FIT:
ϵ_∞ = 1.52
ω_p = 2.38 eV
τ = 0.5 x 10^{-15}
ω_o = 0.48 eV
$[\chi^2]^{1/2}$ = 0.05
R
.45
.40
.35
.30
.25
.20
.15
.10
.05
.00
1000
2000
4000
10000
20000
40000
100000
cm^{-1}


PENN (SN)x DATA : E ⊥ b
• DATA
+ DRUDE FIT:
ϵ_∞ = 1.52
ω_p = 2.38 eV
τ = 0.5 x 10^{-15} sec
$[\chi^2]^{1/2}$ = 0.13
R
.7
.6
.5
.4
.3
.2
.1
.0
1000
2000
4000
10000
20000
40000
100000
cm⁻¹


SHIFT OF REFLECTIVITY MINIMUM
DRUDE: $\epsilon_\infty = 1$
$\omega_p = 5\ eV$
$\tau = 1.7\ eV^{-1}$
LORENTZ: $\omega_o = 7\ eV$
$\omega_p = 10\ eV$
$\tau = 0.7\ eV^{-1}$
R
D
D + L
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
2
4
6
8
10
eV


GAMMA
LAMBD
Z
A
U
E
B
V
D
Y
W
C

SUMMARY OF PARAMETERS DERIVABLE FROM DRUDE FITS AND 1-D TIGHT-BINDING MODEL

ω_p	τ	σ_{opt}	m^* [a]
4.01 eV	0.4×10^{-15} sec	$1313\ (\Omega \cdot cm)^{-1}$	2.6

λ_{ep} (300°K) [b]	d_L	E_W [c]	ξ_0 (0.25°K) [c]
10	246 Å	1.9 eV	24900 Å

ℓ [c]	$\xi = (\ell \xi_0)^{1/2}$	λ [d]	$\kappa = \lambda / \sqrt{2}\,\xi$
1.43 Å	190 Å	20770 Å	77

NOTES:

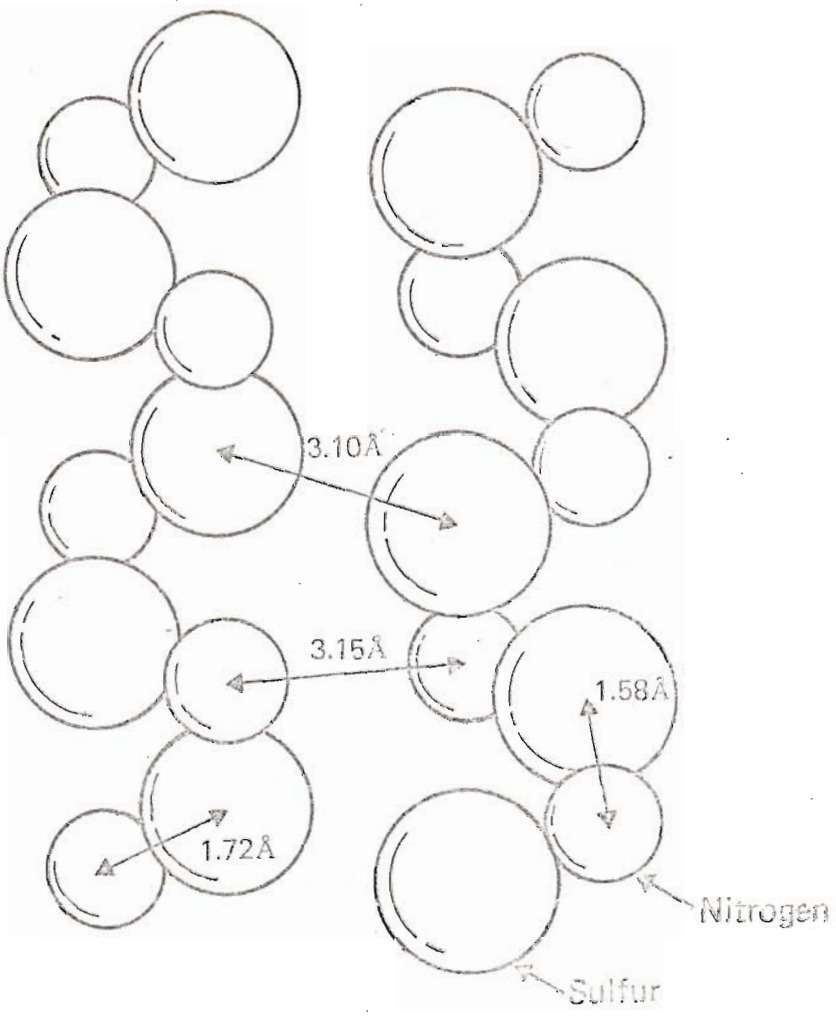
a CAVEAT: ALL CARRIERS (3.05×10^{22}) TAKEN IN ONE BAND

b CAVEAT: ASSUMES DRUDE LIFETIME EQUIVALENT TO ELECTRON-PHONON SCATTERING

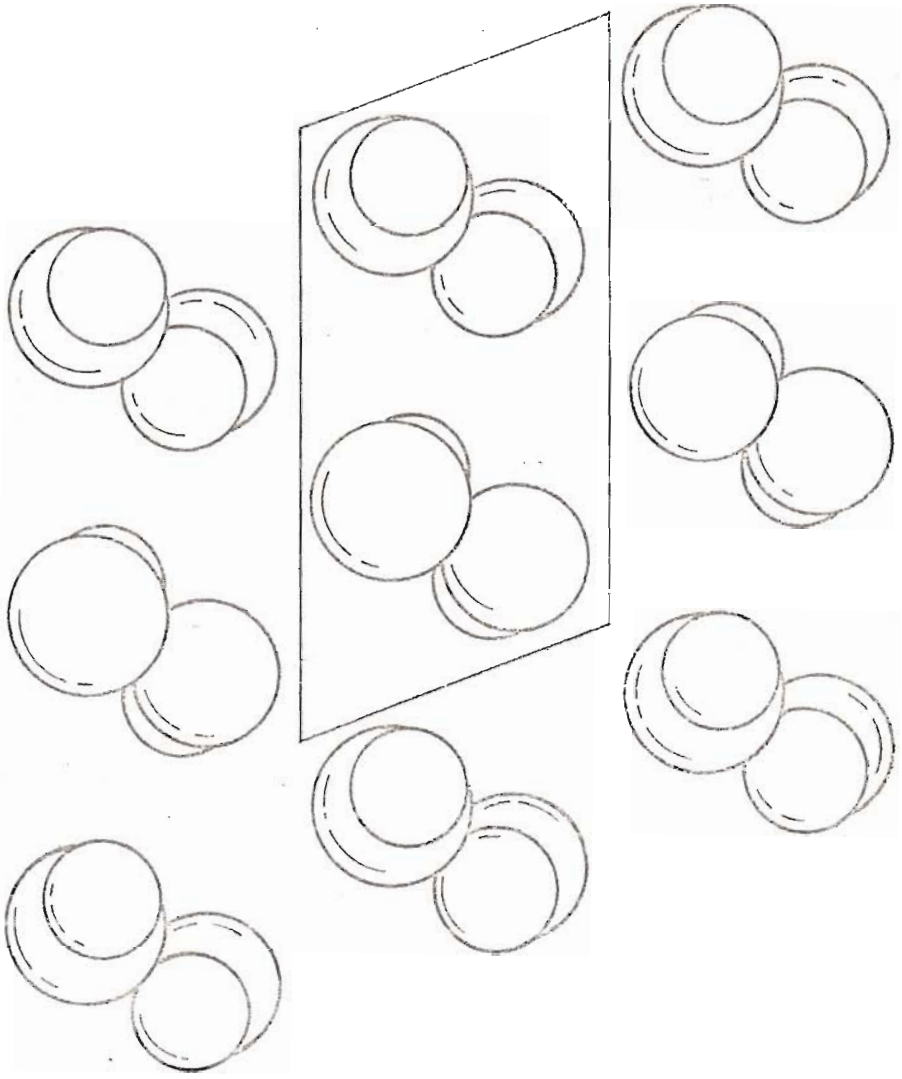
c CAVEAT: ASSUMES 1/2-FILLED, 1-D TIGHT BINDING CONDUCTION BAND WITH (SN) GROUP SEPARATION OF 2.215 Å

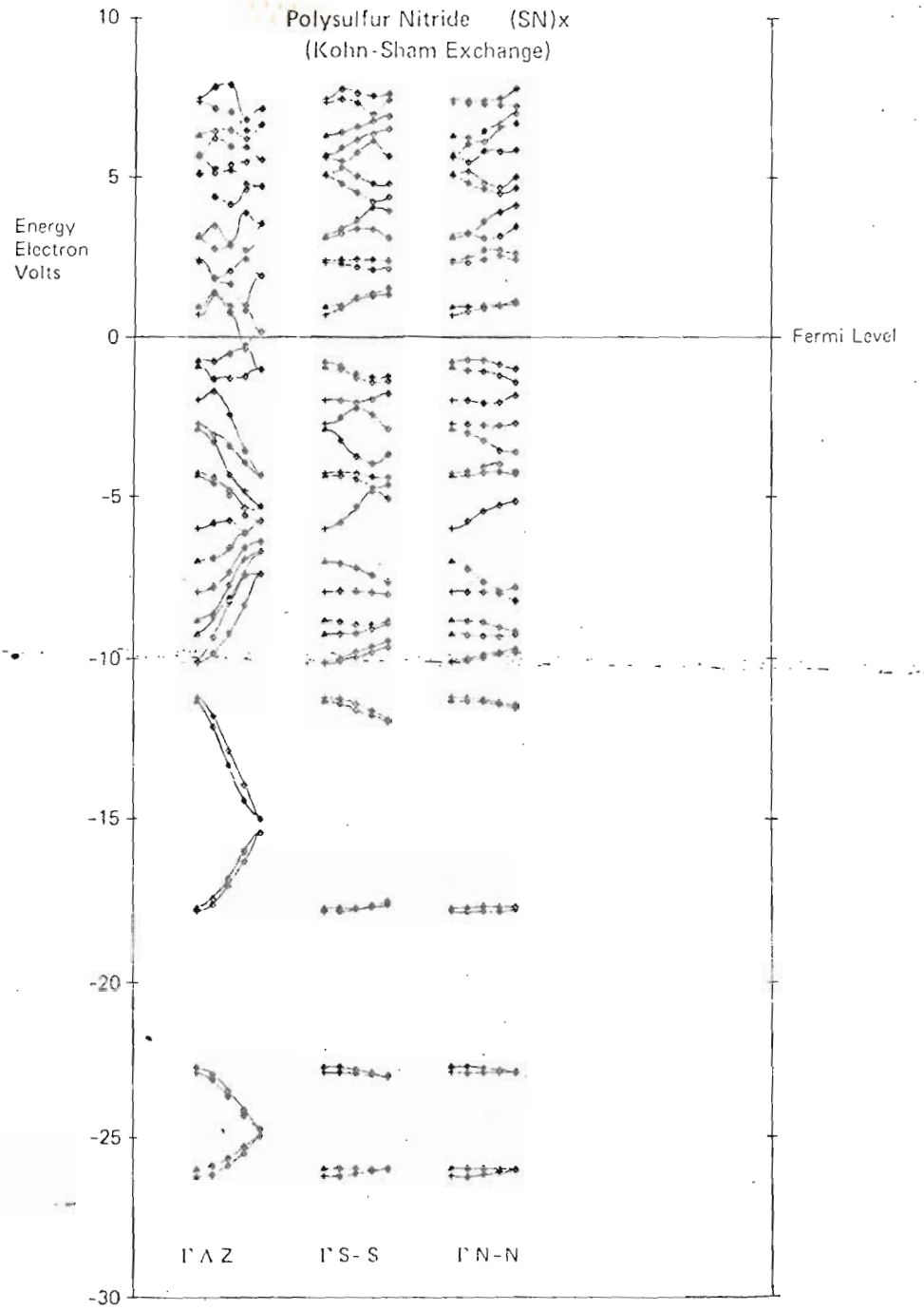
d $\lambda = 0.64\ \lambda_L \left[\xi_0 / \ell\right]^{1/2}$

$(SN)_x$ 2 Chain Segments



$(SN)_x$ Perpendicular to Chain Axis




Polysulfur Nitride (SN)x
(Kohn-Sham Exchange)
Energy
Electron
Volts
10
5
0
-5
-10
-15
-20
-25
-30
Fermi Level
Γ A Z
Γ S-S
Γ N-N