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One-Dimensional Conductors

Thermoreflectance of Organic and Polymeric Metals.

P. M. GRANT, P. MENGEL, E. M. ENGLER, G. CASTRO and
G. B. STREET, IBM Research Laboratory, San Jose, Calif.--

We have examined the thermoreflectance spectrum of $(SN)_x$ crystals and films and of $(TTF)(TCNQ)$ and $(TSeF)(TCNQ)$ crystals in energy ranges appropriate to their Drude properties and low-lying interband transitions as a function of temperature from 300°K to 15°K. In $(SN)_x$, we observe a red shift of the Drude edge which we associate with movement of the Fermi level due to volume effects. Perov and Fischer¹ have reported polarization effects in the thermoreflectance spectrum of $(TTF)(TCNQ)$ connected with the Peierls-Fröhlich transition. We have made similar measurements on $(TSeF)TCNQ$ and compare our results with theirs for $(TTF)(TCNQ)$.

¹P. I. Perov and J. E. Fischer, Phys. Rev. Letters 33, 521 (1974).

Submitted by

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BE 4 Transport Properties of Hg₂.86(AsF₆)₂, R. Spal, T. Wei, C.K. Chiang, A.F. Garito and A.J. Heeger, N. Miro and A.G. MacDiarmid, University of Pennsylvania, Phila., Penna. --We report the temperature dependent dc electrical conductivity of the novel conductor Hg₂.86(AsF₆)₂ which consists of planes of interpenetrating one dimensional chains of Hg atoms. The measured conductivity parallel to the planes is 3.5 x 10³ (Ω-cm)⁻¹ at room temperature and exhibits a negative temperature coefficient down to 4.2K with an anomaly near 220K. Anisotropy measurements using the Montgomery method will be reported in addition. The conductivity measurements will be compared with studies of a plasma edge in the visible optical reflectance and measurements using DSC.

BE 5 Anionic Linear Chain Iridium Carbonyl Halides. A. P. GINSBERG, J. W. KOEPKE, J. J. HAUSER, K. W. WEST, F. J. DI SALVO, C. R. SPRINKLE and R. L. COHEN, Bell Laboratories. --The compounds K_{0.60}Ir(CO)₂Cl₂·0.5H₂O, (TTF)_{0.61}Ir(CO)₂Cl₂ (TTF = Tetrathiafulvalenium), K_{0.57}Ir(CO)₂Br₂·0.2CH₃COCH₃ and Cs_{0.60}Ir(CO)₂Br₂ have been investigated by chemical analysis, infrared and ¹⁹³Ir Mössbauer spectroscopy, electrical conductivity and magnetic susceptibility measurements. Conducting linear chains of cis-[Ir(CO)₂X₂]^{-0.60} (X = Cl, Br) units are shown to be present in these compounds. The apparently well defined compounds K_{0.98}Ir(CO)₂Cl₂·42·0.2CH₃COCH₃ and Na_{0.93}Ir(CO)₂Cl₂·32·0.3CH₃COCH₃ are reformulated as K_{0.60}Ir(CO)₂Cl₂·0.4KCl·0.2CH₃COCH₃ and Na_{0.61}Ir(CO)₂Cl₂·0.32NaCl·0.3CH₃COCH₃, in which the KCl and NaCl are present interstitially in the lattice of linear chains.

BE 6 EPR pair spectra in a dimeric chromium phosphinate.* P. D. KRASICKY, A. L. RITTER, J. C. SCOTT and R. H. SILSBEE, Cornell University. -- The dimeric material, di-μ-diphenylphosphinatoacetylacetonatochromium (III)⁽¹⁾, consists of molecules in which the two chromium atoms, each of spin S_{1,2} = 3/2 are linked by phosphinate (-OP₂O-) bridges, and is therefore the simplest member of the family of one-dimensional poly(chromium phosphinates).⁽²⁾ The "endcapping" acetylacetonate ligands complete the closely octahedral environment of six oxygen atoms around each chromium. Within the molecule the chromium-chromium separation is 5Å, compared to ~10Å between molecules. The EPR pair spectrum at X band indicates an antiferromagnetic exchange, J ≈ 4K, comparable to that in the polymers. At temperatures T < 4K the S=3 (total spin) multiplet is virtually unpopulated, and we have identified transitions within the S=1 and S=2 multiplets. The data are interpreted in terms of a spin Hamiltonian derived by coupling the single ion Hamiltonians with an exchange term.

*Supported by the National Science Foundation.
1C.E. Wilkes and R.A. Jacobson, Inorg. Chem. **4**, 99 (1965).
2J.C. Scott, T.S. Wei, A.F. Garito, A.J. Heeger, H.D. Gillman and P. Nannelli, Proc. Conf. on Magnetism and Magnetic Materials, Phila., 1975 (to be published)

BE 7 UPS Photoemission Properties of (SN)_x. P. MENGEL, W. D. GROBMAN, I. B. ORTENBURGER, P. M. GRANT and B. H. SCHECHTMAN, IBM Research Laboratory, San Jose, Calif. -- We have performed UPS measurements on in situ deposited films of (SN)_x as a function of incident photon energy in the range 7.6 - 40.8 eV. The results are in general agreement with previously reported XPS studies. Relaxation effects lower the observed photoemissive yield at the Fermi level to zero. We analyze our data through comparison with theoretical energy distribution curves obtained from pseudopotential eigenvalues and eigenfunctions. We also report some initial results on the UPS spectrum of partially polymerized S₂N₂.

¹P. Mengel, P. M. Grant, W. E. Rudge, B. H. Schechtman and D. W. Rice, Phys. Rev. Letters **35**, 1803 (1975).

BE 8 XPS Core-Level Spectroscopy, Charge Transfer and Electrostatic Interactions in (SN)_x and Other SN Allotropes. A.J. EPSTEIN, W.R. SALANECK, N.O. LIPARI and J.W-p LIN, Xerox Webster Research Center, Webster, N.Y. 14580. --The binding energies of S_{2p} and N_{1s} levels in (SN)_x have been studied via x-ray photoemission spectroscopy and results compared with neutral S₈ and N₂ molecules respectively, as well as S₄N₄. The effective charge transfer from sulfur to nitrogen is 0.5|e| in (SN)_x as compared to 0.6|e| in S₄N₄. Shake-up structure on the core level lines of (SN)_x is assigned to excitation of conduction electron plasmons. Using the above XPS measured net charges, the electrostatic interactions in S₂N₂, S₄N₄ and (SN)_x were calculated. Though the total electrostatic potential at any site due to all other atoms in a crystal is large and nearly identical for all three allotropes, the net electrostatic interaction between molecules (polymer chains) is small and nearly identical in all three cases.

BE 9 Thermoreflectance of Organic and Polymeric Metals. P. M. GRANT, P. MENGEL, E. M. ENGLER, G. CASTRO and G. B. STREET, IBM Research Laboratory, San Jose, Calif. -- We have examined the thermoreflectance spectrum of (SN)_x crystals and films and of (TTF)(TCNQ) and (TSeF)(TCNQ)_x crystals in energy ranges appropriate to their Drude properties and low-lying interband transitions as a function of temperature from 300°K to 15°K. In (SN)_x, we observe a red shift of the Drude edge which we associate with movement of the Fermi level due to volume effects. Perov and Fischer¹ have reported polarization effects in the thermoreflectance spectrum of (TTF)(TCNQ) connected with the Peierls-Fröhlich transition. We have made similar measurements on (TSeF)(TCNQ) and compare our results with theirs for (TTF)(TCNQ).

¹P. I. Perov and J. E. Fischer, Phys. Rev. Letters **33**, 521 (1974).

BE 10 Calculated Optical Properties of (SN)_x. I. B. ORTENBURGER, W. E. RUDGE and P. M. GRANT, IBM Research Laboratory, San Jose, Calif. --The tensorial dielectric constant ε_{ij}(ω) and the tensorial photoemission yield D(E,ω) have been calculated for (SN)_x using a pseudopotential interpolation scheme based^x on a first principles OPW band structure. D(E,ω) and ε_{ij}(ω) were computed by the Gilat-Raubenheimer zonal integration method. Our results will be compared to experimental photoemission and optical measurements on randomly oriented (SN)_x films.

¹A. A. Bright and A. F. Garito, to be published.

BE 11 Molecular Cluster and Band Structure Calculations for (SN)_x. D. R. SALAHUB and R. P. MESSMER, General Electric. --Molecular cluster and band structure calculations for (SN)_x show that (i) a single (SN)_x chain should be a Peierls insulator, (ii) semi-metallic behavior is brought about by interchain coupling which moves the Fermi level from the Peierls gap to a place where it intersects two bands, (iii) the most important interactions occur in a 100 plane, and not as previously assumed in a 102 plane. Important aspects of the electronic structure of intermediates involved in the polymerization and sublimation of (SN)_x are also discussed.

BE 12 Band Structure, Density of States, and Fermi Surface Topology of the (SN)_x Crystal.* W. Y. CHING, J. G. HARRISON, and CHUN C. LIN, U. of Wisconsin-

Outline of BE9: "Thermoreflectance of Organic and Polymer Metals"

- Thermoreflectance is a form of derivative spectroscopy which has frequently been applied to conventional metals to help elucidate details of their electronic structure difficult to obtain by other methods. The experiment consists of indirectly heating the sample via periodic current pulses passed through a gold film in thermal contact with it and phase detecting the impressed modulation in the reflectivity.
- In this talk we will discuss mostly $(\text{SN})_x$ and, if time permits, some of our results for (TSeF) (TCNQ) as well.
- Our $(\text{SN})_x$ studies were motivated by our finding a very weak temperature dependence of the reflection spectrum of $(\text{SN})_x$ crystals.
 - Change in E_{dc} of 6 observed over the same temperature range.
 - Change of E_{dc} of ~ 6 eV for $P \rightarrow 10$ kbar
 - Suggests little or no relation of E_{dc} to optical properties
- Equations for thermoreflectance
 - For many metals, $\Delta R_p / \Delta T$ dominated although no a priori reason to assume same for $(\text{SN})_x$.
 - In any event, the gross movement of the reflectivity with temperature will determine the sign of $\Delta R / R$.

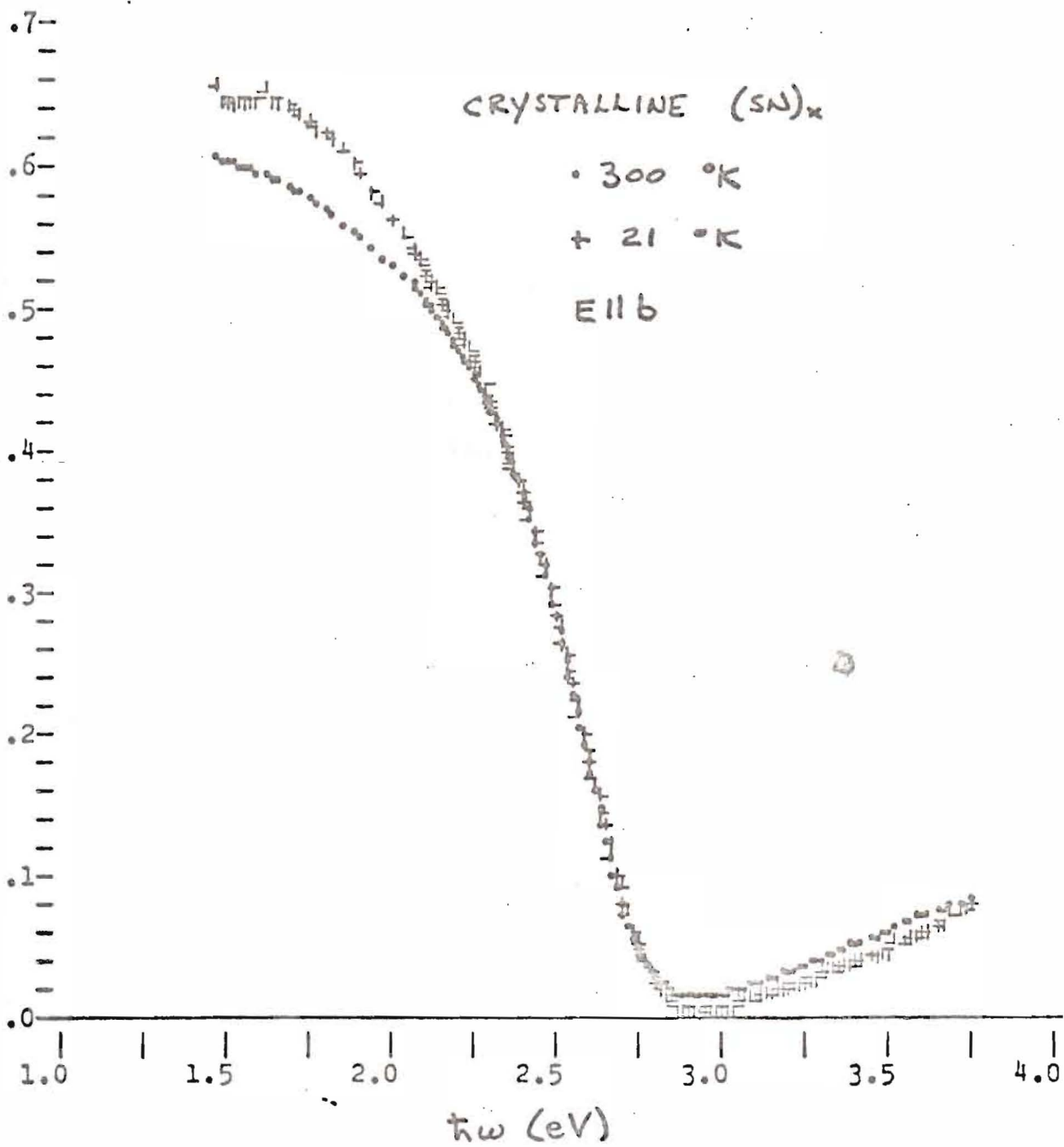
$\Delta R_p / \Delta T = 9.6 \times 10^{-5} / 0.6$
 $\Delta R_p / \Delta T = 1.38 \times 10^{-5} / 0.6$

(2)

- $(SN)_x$ Film Thermoreflectance in Druide Range
 - Shows red shift in both sign and direction of plasma energy, connection with T_{dc} now even more enigmatic.
- Reasons why $(SN)_x$ optical properties do not connect with T_{dc} :
 - Answer probably lies in the difference in the temperature or dilation dependence of the two lifetimes governing dc and optical.
 - Relatively strong optical phonon bands lie in the wavelength range 5-10 μ . It is reasonable to assume strong temperature independent damping from these phonons could be the dominant factor at optical frequencies.
 - If the dc scattering is dominated by electron-electron effects, as suggested by Chiang and coworkers, this interaction could be greatly affected by changes in the shape of the Fermi surfaces due to dilation, particularly in the interchain directions, which could also produce the small optical red shift in plasma energy yet leave the optical lifetime unaffected. We will be investigating this possibility through computer simulation of lattice dilation effects on the $(SN)_x$ Fermi surface.
- Interband Effects in $(SN)_x$ Film Thermoreflectance
 - Does not arise from E_{11b} ϵ_2 structure
 - Does arise from E_{1b} (T_{02}) ϵ_2 structure
 - DR/R traditionally sensitive to interband effects.
- Conclusions:
 - Weak temperature dependence of ω_p and T_{osc} suggests T_{dc} temperature dependence completely dominated by different τ .

(3)

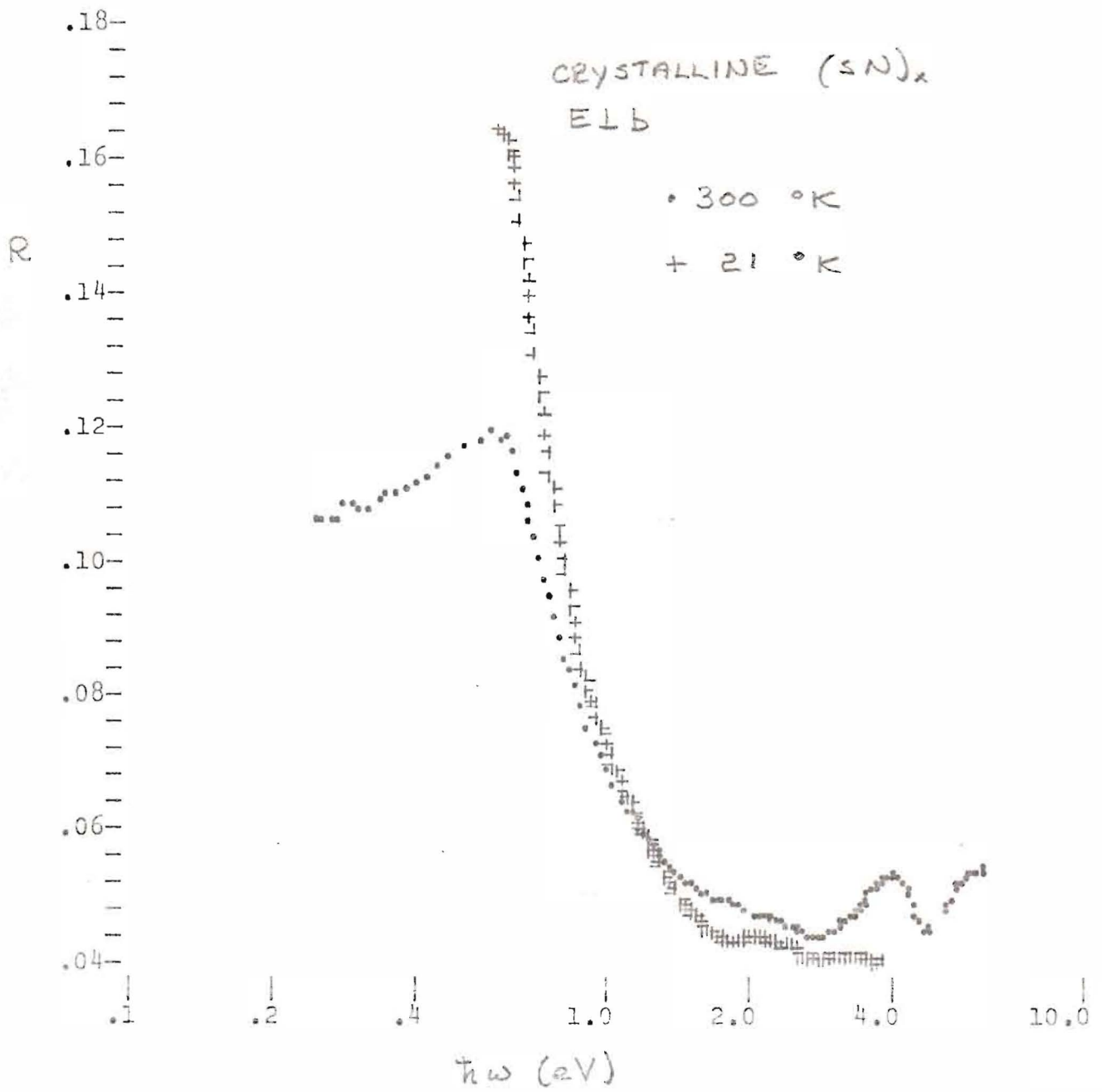
- (TSeF) (TCND) Thermoreflectance Results.
 - Review briefly Perov and Fischen results
 - Show same behavior for (TSeF) (TCND)



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THERMOREFLECTANCE EQUATIONS

$$\frac{1}{R} \frac{\Delta R}{\Delta T} = \left(\frac{\partial \ln R}{\partial \epsilon_1} \right) \frac{\Delta \epsilon_1}{\Delta T} + \left(\frac{\partial \ln R}{\partial \epsilon_2} \right) \frac{\Delta \epsilon_2}{\Delta T}$$

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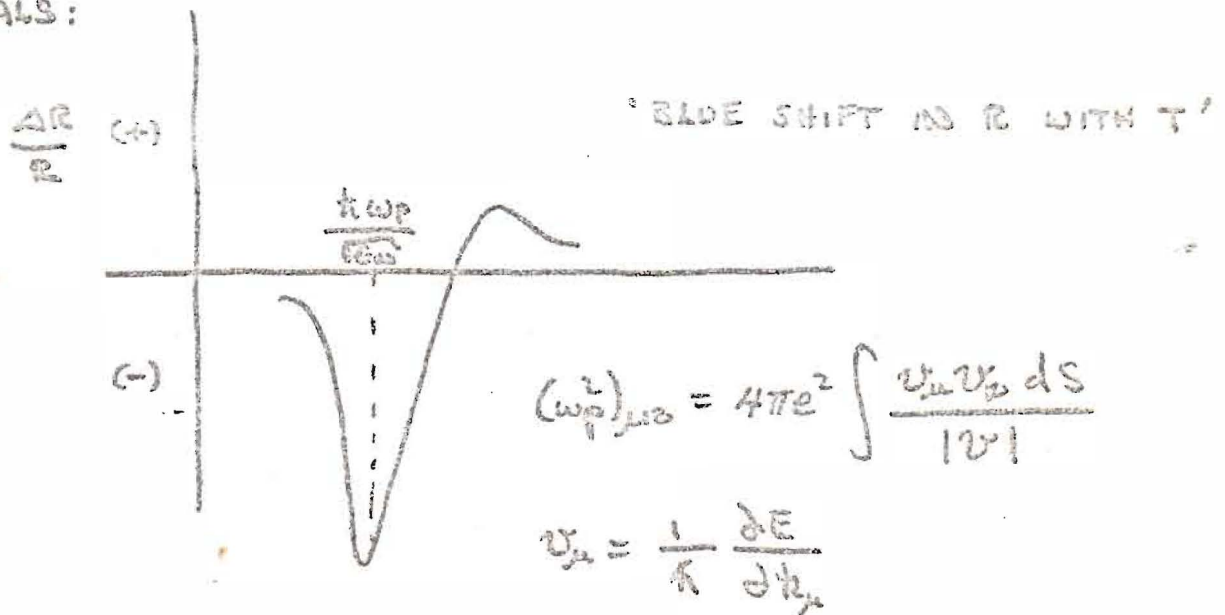
$$\beta_1(\epsilon_1, \epsilon_2) \qquad \qquad \qquad \beta_2(\epsilon_1, \epsilon_2)$$

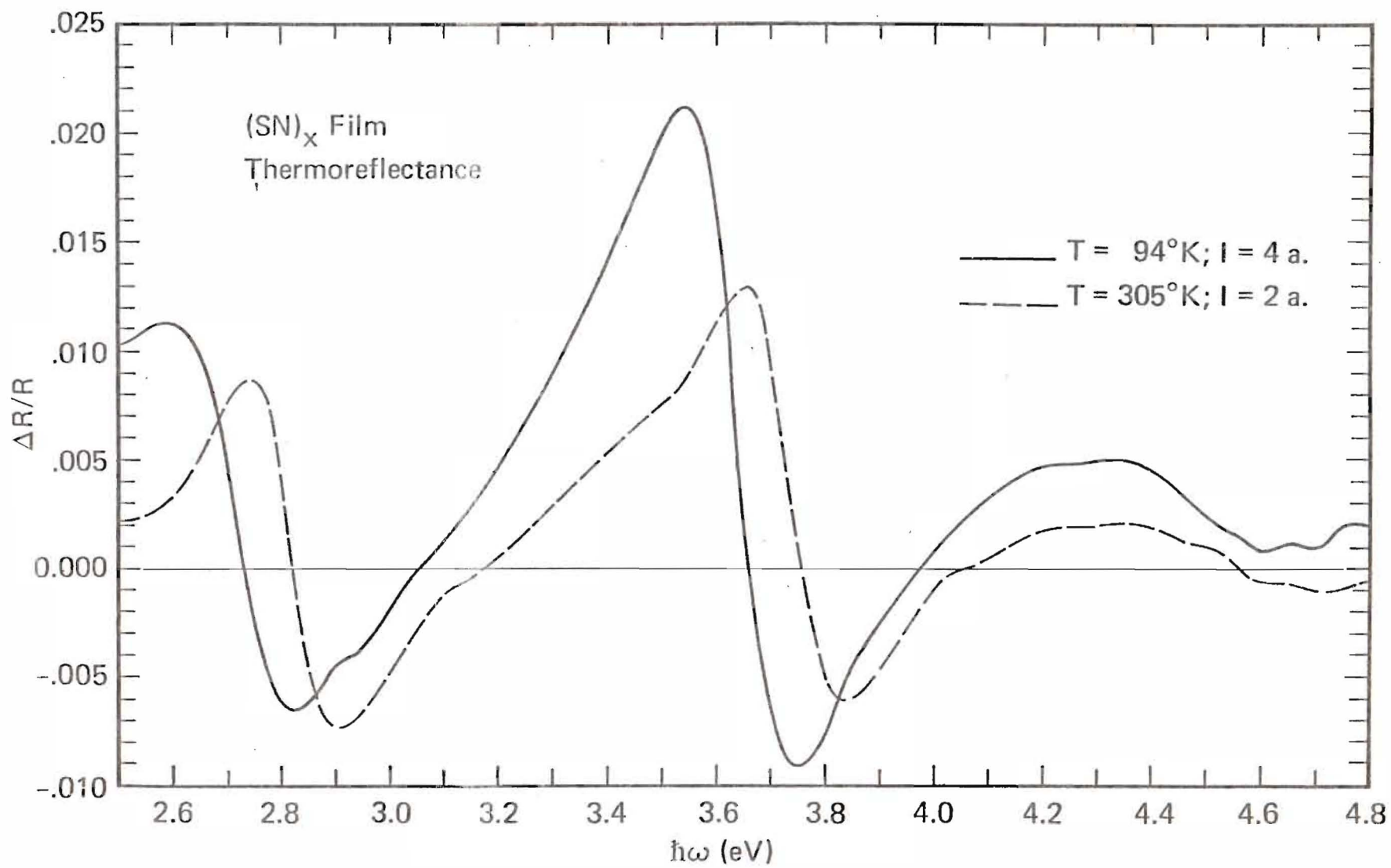
$$\frac{\Delta \epsilon_{1,2}}{\Delta T} = \frac{\partial \epsilon_{1,2}}{\partial \omega_0} \frac{\Delta \omega_0}{\Delta T} + \frac{\partial \epsilon_{1,2}}{\partial \omega_p} \frac{\Delta \omega_p}{\Delta T}$$

$$+ \frac{\partial \epsilon_{1,2}}{\partial \gamma} \frac{\Delta \gamma}{\Delta T} + \frac{\partial \epsilon_{1,2}}{\partial \epsilon_\infty} \frac{\Delta \epsilon_\infty}{\Delta T}$$

$$\epsilon(\omega) = \epsilon_\infty + \frac{\omega_p^2}{\omega_0^2 - \omega^2 + i\omega/\rho}$$

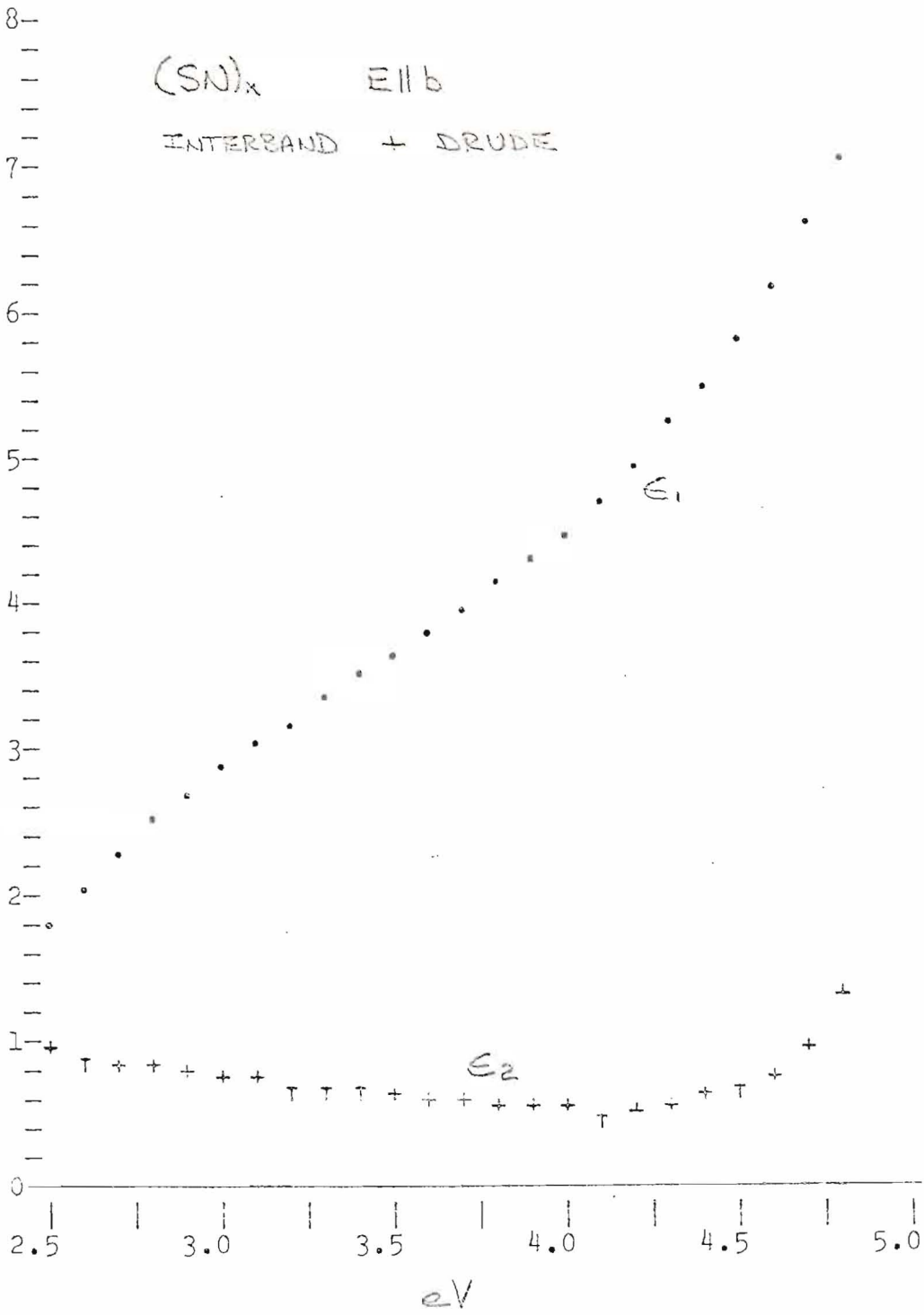
FOR METALS:





(SN)_x E11b
INTERBAND + DRUDE

ϵ_1, ϵ_2



ϵ_1, ϵ_2

(SN)_x ELb (T02)
INTERBAND + DRUDE

