

Abstract Submitted

for the Atlanta Meeting of the
American Physical Society
March 29 - April 1, 1976

Physics and Astronomy
Classification Scheme
Number 71.20

14

Bulletin Subject Heading
in which paper should be placed
(SN)_x

965-IBM-185

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.¹ Re-
laxation 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 eigen-
functions. 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
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Submitted by .

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965-IBM-185

APS News — p. 210

bulletin

OF THE AMERICAN PHYSICAL SOCIETY

MARCH 1976

INCLUDING THE PROGRAM OF THE
1976 MARCH MEETING IN ATLANTA, GA.

29 MARCH — 1 APRIL 1976

Series II, Vol. 21, No. 3 (1976)

pp. 209-488

MGR166160 5APS
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I B M RESEARCH LABS
MONTEREY & COTTLE RDS
SAN JOSE CA 95193

021003 10

PUBLISHED FOR THE AMERICAN PHYSICAL SOCIETY
BY THE AMERICAN INSTITUTE OF PHYSICS

965-118M-101

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 $3.5 \times 10^3 (\Omega\text{-cm})^{-1}$ 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. KOEFKE, 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 phosphate.* 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 phosphate (-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. 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) 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 ε₂(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 ε₂(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

Photoemission talk

We carried out x-ray and UPS photo-emission measurements on $(\text{SN})_x$ films to reveal experimentally the electronic properties of this compound and compare it with theoretical calculations.

In this talk we would like to concentrate on the result for the valence band region of $(\text{SN})_x$.

The first slide gives an overall picture of the valence band region of $(\text{SN})_x$. The upper part shows the experimental data from XPS measurement (Al K α 1.4 keV line, dots raw data, solid line inelastic background

subtracted). The lower part gives a comparison

with 2 different theoretical DOS, 1D TB

(T & P) and 3D OPW (R & G). The valence band

extends about 30 eV below E_F , and we find a good qualitative agreement between both theoretical calculations and the experimental data, and in addition the

3D OPW gives a good quantitative agreement

in peak energy position and relative peak intensity too.

In the UPS measurements we hoped with better resolution to clarify the structure near the Fermi level, density of state appears to be low, the exact energy position of peak 1, which shows the coincidence in energy with the EDOPW only for the Boudoule crystal structure.

The next slide shows EDC's obtained from a continuously H_2 lamp for eleven photocurrents between 7.6 and 11.1 eV. The cross line indicates zero kinetic energy. The solid curves are the experimental results, dashed are theoretical EDC calculations.

The films have been prepared in-situ of the UHV chamber. After the measurement we took them out for X-ray analysis, which shows the (102) plane in a rotating-crystal method type of experiment. This gives evidence for a preferred orientation in the films but

this may be still a disorder in the direction perpendicular to the chain axes.

The EDC's are in general agreement with XPS measurement. The peaks at 1.0 eV and 4.5 eV

correspond to peak 1 and 2 in the slide before, relative intensity of the second peak appreciable higher, and there is an additional structure at about 2.5 eV. Surprising again is the low density of state at the Fermi level (nearly zero).

The theoretical EDC's (dashed line) are calculated from first principle pseudopotential eigenvalues and eigenfunctions.

The experimentally found workfunction of 4.2 eV was used for ^{applying} a step-like escape probability function on each of the theoretical EDC's.

The theoretical calculation are in reasonably agreement with the

the lower photon energies. All structure in the exp. curves present in the calculation, emphasize that we used the Penn structure, which we believe is the more appropriate structure, but the correlation in energy position of peaks is much better with the Bandville structure. Most important is that also the calculated EDC show a very low density of state at E_F . Now we can clearly show that this is due to Matrix element effect, which gives a very low transition probability near the Fermi level, about $1/5$ of the average matrix element. The increase of the DOS ^{at higher photon energies} in the theoretical calculation is not found in the experimental data. In the theory the reason is artificial final state effect and we believe that the pseudopotential method is ^{just} insufficient in determining the conduction bands far above

the Fermi level.

Indeed measurements with higher photon-energies, which are shown in the next slide for 10.2, 6.8, 21 and 40.8 eV show again a low density of state at the Fermi level. Again we see the same structure obtained at the other photon energies, and the bottom curves give a comparison with a pseudopotential DOS.

Instead of a increase of the DOS at E_F , we even get a gap of 0.2 eV at the Fermi level; and there are some reasons to believe, that the films exist in a non fully developed crystalline phase - perhaps amorphous considering the order perpendicular to the chain axes. (reasons: conductivity, reflection measurement, structure analysis)

In this case the films are most disordered at the surface and therefore depending on the process used in the

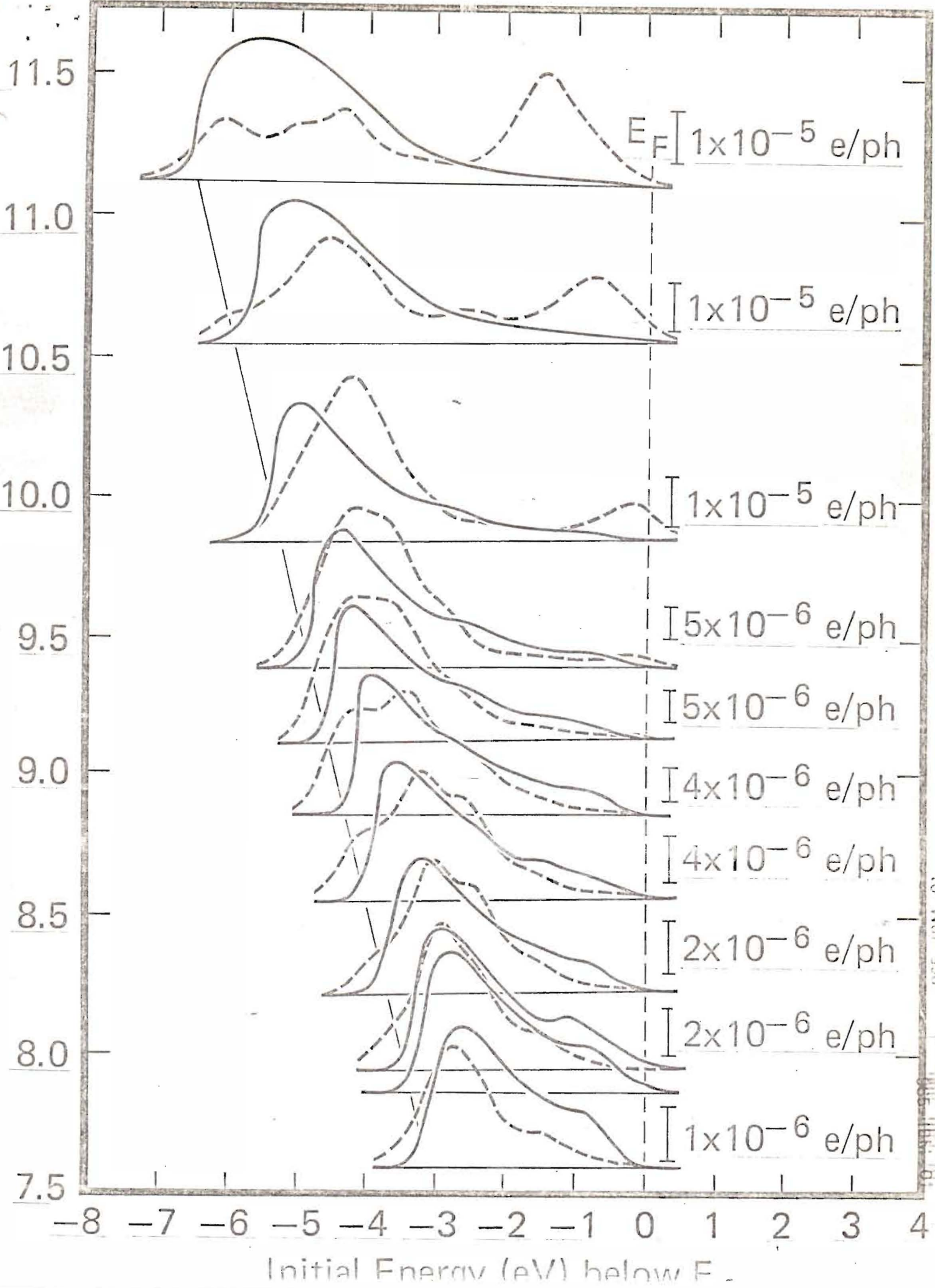
photoemission experiment, as gap opens
at photon energies where the escape length
has it's minimum.

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