conductor Ge is, of course, much different from that of Cu or Zn, we nevertheless expect it to show a resonant satellite.

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[1] R. E. Dietz, E. G. McRae, Y. Yafet, and C. W. Caldwell, Phys. Rev. Lett. 33, 1372 (1974); E. J. McGuire, J. Phys. Chem. Solids 33, 577 (1972).

[2] D. R. Penn, Phys. Rev. Lett. 42, 921 (1979).

[3] C. Guillot, Y. Ballu, J. Paigné, J. Lecante, K. P. Jain, P. Thiry, R. Pinchaux, Y. Pétroff, and L. M. Falicov, Phys. Rev. Lett. 39, 1632 (1977).

[4] M. Iwan, F. J. Himpsel, and D. E. Eastman, Phys. Rev. Lett. 43, 1829 (1979).

[5] E. Antonides, E. C. Janse, and G. A. Sawatzky, Phys. Rev. B 15, 1669 (1977); G. A. Sawatzky, Phys. Rev. Lett. 39, 504 (1977).

[6] P. Nozières and C. T. de Dominicis, Phys. Rev. 178, 1097 (1969).

[7] L. C. Davis and L. A. Feldkamp, J. Appl. Phys. 50, 1944 (1979).

[8] U. Fano, Phys. Rev. 124, 1866 (1961).

[9] L. C. Davis and L. A. Feldkamp, Phys. Rev. B 15, 2961 (1977).

[10] A. Kotani and Y. Toyozawa, J. Phys. Soc. Jpn. 37, 912 (1974).

[11] C. A. Swarts, J. D. Dow, and C. P. Flynn, Phys. Rev. Lett. 43, 158 (1979); J. D. Dow, Nouvo Cimento 39B, 465 (1977); J. D. Dow and C. P. Flynn, to be published.

[12] P. W. Anderson, Phys. Rev. 164, 352 (1967).

[13] Equations (11) and (13) can be generalized to include the direct excitation of the satellite and the additional absorption due to d-band holes as, for example, in Ni.

Band Theory of Metallic Polyacetylene

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Ab initio extended muffin-tin orbital calculations are presented for *trans*-polyacetylene heavily doped with AsF_5, AsF_6, SbF_6, or PF_6. For the hexafluoride dopants, AsF_6 and SbF_6, hybridization of metal s states with polymer π states produces a partly filled metallic band. This provides a band model of metallic conductivity within and between chains consistent with anisotropic electric conductivity. This model should also apply to other doped conjugated polymers.

It has recently been discovered that doping can vary the electric conductivity of *trans*-polyacetylene $[t\text{-}(CH)_x]$ by about twelve orders of magnitude.[1,2] The highest conductivities ($2000\ \Omega^{-1}\ \text{cm}^{-1}$) were observed after doping with 10% AsF_5 $\{t\text{-}[CH(AsF_5)_{0.1}]_x\}$. AsF_5 and I_2 dopants have been most widely used but other halides and metal ions are also effective. For all these dopants, an abrupt semiconductor-metal transition takes place at 1–2% doping, and metallic conductivity is observed up to 20% doping. Recent x-ray absorption experiments[3] indicate that exposing $t\text{-}(CH)_x$ films to AsF_5 vapor actually leads to incorporation of AsF_6^- as the effective dopant. ESR measurements[4,5] indicate that the charge carriers in lightly doped p-type semiconducting samples are not the usual free holes seen in inorganic semiconductors. Finally, other conjugate polymers are reportedly dopable up to metallic levels of conductivity.[6-8]

We present results of first-principles extended muffin-tin orbital (EMTO)[9,10] calculations on pure, defect-free $t\text{-}(CH)_x$, and on doped materials, denoted $t\text{-}(CHA_y)_x$, in the high doping regime, $y = \frac{1}{6}$. Dopants, A, studied are AsF_5, AsF_6, SbF_6, and PF_6. Our results show that heavy doping by AsF_6 and SbF_6 produces partly filled metal s bands which imply strong metallic conductivity along chains and weaker metallic conductivity between chains. Similar doping with AsF_5 yields a semiconductor with a completely filled As s valence band 2 eV below an empty C=C π conduction band. $t\text{-}[CH(PF_6)_{1/6}]_x$ is different in that its P s band is empty; charge transfer to F atoms partly empties a π band and implies metallic conductivity along, but not between, chains. This simple one-electron picture (a) explains anisotropic metallic conductivity; (b) substantiates the conclusion that AsF_6^- is the effective dopant in highly conducting $t\text{-}(CH)_x$ films; and (c) predicts qualitatively different properties for samples doped with PF_6.

Crystalline $cis\text{-}(CH)_x$ is known to have an orthorhombic unit cell containing two chains.[11] The structure of t-(CH)$_x$ has not been completely characterized.[12] We have modeled the doped polymer, t-(CH$A_{1/6}$)$_x$, by an orthorhombic unit cell containing one unit of dopant and one chain of 6 CH units. This is three times the length of the t-(CH)$_x$ unit cell. We have used C-C, C=C, and C-H bond lengths of 1.46, 1.34, and 1.09 Å, respectively.[8] The C-C-H bond angle is 120° and the C=C-C angle is 125°.[8] Sb-F, As-F, and P-F bond lengths are 1.95, 1.77, and 1.57 Å, respectively. The unit cell is taken to be 7.51 Å in x, 7.00 Å in y, and 6.90 Å in z, where x is along the chain direction and y and z axes connect adjacent parallel chains. Fluoride dopants are positioned between two parallel chains so that one F atom is directly above the center of a C=C bond in each chain. The hexafluoride dopants are square bipyramidal; AsF$_5$ is triangular bipyramidal. We have varied C-to-F interaction by adjusting the dopant position in the unit cell, by varying the z dimension of the unit cell, and by rotating the dopant with respect to the polymer chains. This model allows us the flexibility to compare different dopants and effects of different dopant-polymer orientations.

Our EMTO calculations[9,10] use a first-principles potential calculated from overlapping atomic charge densities [exchange parameter $\alpha = 1.0$ (Ref. 13)]. No spherical approximations to the potential are used. This method has been successfully applied to the calculations of energy levels and charge densities for isolated molecules,[10] undoped polymers,[14] and molecule-surface interactions.[10] To establish our model doping structure, we first apply the EMTC method to undoped t-(CH)$_x$. The highest occupied (π) and lowest unoccupied (π^*) bands are shown in Fig. 1(a). Because of our large unit cell, the Brillouin zone is $\frac{1}{3}$ as long as the primitive unit cell, so that there are three bands each for the π and π^* states. Our calculated band gap is 1.6 eV, in good agreement with experimental estimates 1.4–1.9 eV.[1] The flat bands from U to X (perpendicular to the chain direction) are consistent with the observed anisotropic conductivity.[1,2] The band-gap minimum is at the zone edge of the primitive unit cell. This agrees with the picture of a band gap arising from alternating single- and double-bond lengths driven by a Peierls distortion.[15,16] First-principles extended tight-binding calculations[16] have found zone-edge band gaps of 0.8 and 2.3 eV using, respectively, less and more bond alternation than we use here. An extended Hückel calculation has found a zone-edge band gap of 0.96 eV.[17] A CNDO/2 calculation found a zone-center band gap of 7.455 eV,[18] and simple Hückel theory predicts a vanishingly small band gap for very long conjugated chains.[4,5,19] The present model clearly agrees with experiment at least as well as any previous calculation.

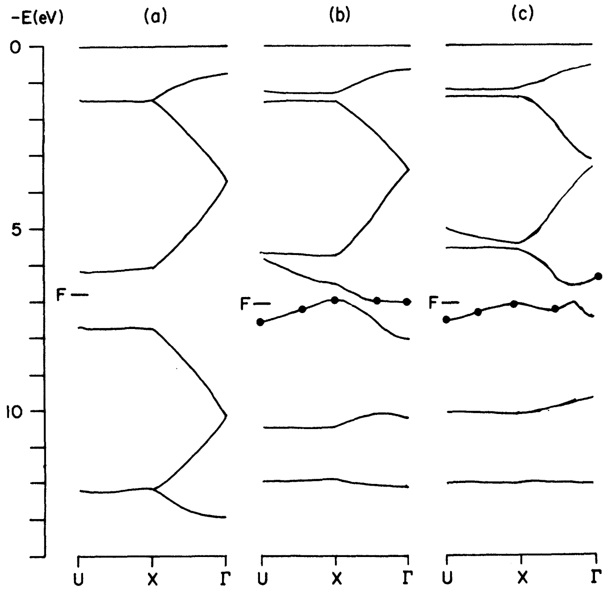

FIG. 1. Energy bands of (a) t-(CH)$_x$; (b) t-[CH(AsF$_6$)$_{1/6}$]$_x$, with AsF$_6$ symmetrically placed between two t-(CH)$_x$ chains; (c) t-[CH(AsF$_6$)$_{1/6}$]$_x$, with AsF$_6$ asymmetrically placed. F denotes Fermi energy; circles denote states which are predominantly As s levels. Γ, X, and U denote the $\vec{k}$ points (0, 0, 0), (π/a, 0, 0), and (π/a, 0, π/c), respectively.

Figures 1(b) and 1(c) show the effects of doping with AsF$_6$ (47 valence electrons) and the effect of varying F-to-C distances. In Fig. 1(b) the dopant is placed symmetrically between parallel t-(CH)$_x$ chains, with F-to-C distances of 1.81 Å in both directions. An As s band, denoted by dots, has hybridized with, and pushed up, the highest C=C π band. This s band is half filled, as in a metal. Its dispersion in the x direction results from hybridization with the C=C π band: Direct overlap between s orbitals on As atoms 7.51 Å apart is negligible. The s-band dispersion in the z direction is about equal to the dispersion in the x direction. This implies metallic interchain conductivity, as well as intrachain conductivity. Figure 1(c) shows bands for AsF$_6$ asymmetrically placed with F-to-C distances of 1.60 Å to one chain and 2.02 Å to the other. The effect of asymmetry is to reduce s-band dispersion a little in the z direction. Changing the F-to-C distance primarily affects the separation between the highest π band and the s band. Our assumed structure does not accurately represent the generally accepted geometric relationship between adjacent $(\mathrm{CH})_x$ chains, in which neighboring planes are canted by about 50° with respect to the c crystallographic axis and nearly orthogonal to each other along a.[11] In order to simulate the effects of such a rearrangement on our model, we performed a calculation where the $\mathrm{AsF_6}$ was rotated 15° relative to the polymer chains. We found the change to decrease only slightly the As-s-band to C=C-band overlap. Thus, for a range of reasonable F-to-C interactions, metallic bands are produced parallel and perpendicular to the chains. As a fiber contains finite length chains, interchain conductivity is necessary for a metallic behavior of the whole fiber. This picture of interchain conductivity is consistent with measured cross-fiber conductivities of $\sim 10^2\ \Omega^{-1}\ \mathrm{cm}^{-1}$, the lower end of the metallic range.[1,2] This picture is quite distinct from the rigid-band model proposed by Grant and Batra in which interchain conductivity at low doping levels occurs through the finite overlap of adjacent chains.[16]

Figure 2(a) shows the very different effects of doping with $\mathrm{AsF_5}$ (40 valence electrons). Here, as in Fig. 1(c), the F-to-C distances are 1.60 and 2.02 Å. Now the As s band is flat and completely filled. The highest π band is pushed 2 eV above the s band and is completely empty. These bands are characteristic of a wide-band-gap semiconductor and incompatible with metallic conductivity. Figures 1(b), 1(c), and 2(a) support the conclusion from x-ray absorption data[3] that absorption of $\mathrm{AsF_5}$ into t-$(\mathrm{CH})_x$ is followed by disproportionation to $\mathrm{AsF_6}^-$ and $\mathrm{AsF_3}$. A separate experiment showed[3] that $\mathrm{AsF_3}$ is weakly absorbed and does not significantly increase conductivity. Since the As s level in $\mathrm{AsF_3}$ is already completely filled, our model also predicts ineffective doping by $\mathrm{AsF_3}$. Both theory and experiment therefore conclude that highly conducting samples are effectively doped with $\mathrm{AsF_6}^-$. This is further supported by Raman experiments[20] indicating that doping with $\mathrm{I_2}$ or $\mathrm{Br_2}$ results in disproportionation to $\mathrm{I_3}^-$ or $\mathrm{Br_3}^-$ as the effective dopants in t-$(\mathrm{CH})_x$. $\mathrm{AsF_5}$ disproportionation to $\mathrm{AsF_6}^-$ has also been observed in graphite.[21]

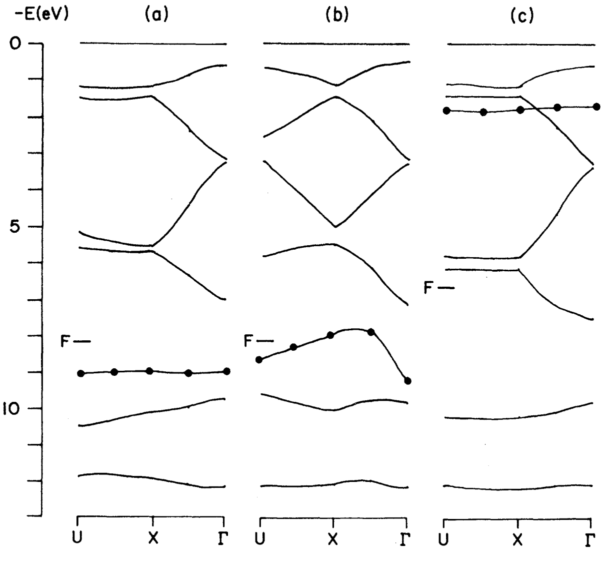

FIG. 2. Energy bands of (a) t-$[\mathrm{CH(AsF_5)}_{1/6}]_x$, (b) t-$[\mathrm{CH(SbF_6)}_{1/6}]_x$, and (c) t-$[\mathrm{CH(PF_6)}_{1/6}]_x$. Labeling conventions as in Fig. 1.

For completeness, the dopants $\mathrm{SbF_6}$ and $\mathrm{PF_6}$ have also been investigated. Results are shown in Figs. 2(b) and 2(c). The F-to-C distances are 1.60 and 1.69 Å for $\mathrm{SbF_6}$. This choice of distances produces strong hybridization and overlap between the half-filled Sb s band and the C=C π band. Like $\mathrm{AsF_6}^-$, $\mathrm{SbF_6}^-$ produces metallic conductivity along and between chains. For doping with $\mathrm{PF_6}$ the F-to-C distances were taken to be 1.60 Å with both neighboring chains. The bands, shown in Fig. 2(c), are very different from those in Fig. 1(b). The P s band is empty and lies among the π^* bands. Perturbation by the dopant has half emptied the highest π band. This band is flat and empty in the z direction. Metallic intrachain conductivity and insulating interchain coupling are expected. Poor conductivity has been observed when t-$(\mathrm{CH})_x$ is doped with $\mathrm{PF_6}$.[22]

Consider now how our results might apply to the low-doping regime and to other doped conjugated organic polymers. All our calculations show charge transfer producing a cationic chain in contact with an anionic dopant. Similar charge transfers probably occur with low doping. This transfer may be expected to create a mobile, spin-$\frac{1}{2}$ hole in the valence band. Since ESR data have indicated that the charge carriers are spinless,[4,5] it has recently been proposed that the charge transfer could form a charged soliton of spin zero instead of the free hole.[23,24] Our model provides a mechanism for the charge transfer, but makes no prediction about soliton formation.

Our mechanism for metallic conductivity depends on charge transfer from a C=C bond to produce a partly filled dopant level. It also depends on hybridization with this band to produce dispersion of the metallic band in directions along and between chains. Polymer-dopant separation affects dispersion but not filling of the metallic band. Because C p states participating in π bonding are relatively reactive, we expect the present mechanism to be very general. It should apply to other doped conjugated polymers[6-8] which lack the resonant ground states necessary for soliton formation.

In summary, we have (1) presented the first band theoretic treatment of doped polymers; (2) provided the first detailed picture of metallic conductivity arising from heavy doping; (3) explored the relative importance of dopant identity and dopant-polymer separation; (4) proposed mechanisms for interchain as well as intrachain conductivity, consistent with observed anisotropy; (5) shown that our results are compatible with low-doping ESR measurements; and (6) argued that the present model of conductivity should be applicable to other doped conjugated polymers.

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[1] C. K. Chiang, A. J. Heeger, and A. G. MacDiarmid, Ber. Bunsenges. Phys. Chem. 83, 407 (1979), and references cited therein.

[2] Y. W. Park, M. A. Druy, C. K. Chiang, A. J. Heeger, A. G. Mac Diarmid, H. Shirakawa, and S. Ikeda, Polym. Lett. 17, 195 (1979).

[3] T. C. Clarke, R. H. Geiss, W. D. Gill, P. M. Grant, H. Morawitz, G. B. Street, and D. E. Sayers, to be published.

[4] H. Shirakawa, T. Ito, and S. Ikeda, Makromol. Chem. 179, 1565 (1978).

[5] I. B. Goldberg, H. R. Crowe, P. R. Newman, A. J. Heeger, and A. G. MacDiarmid, J. Chem. Phys. 70, 1132 (1979).

[6] H. Naarmann, Ber. Bunsenges. Phys. Chem. 83, 427 (1979).

[7] R. C. Teitelbaum, T. J. Marks, and S. L. Ruby, Bull. Am. Phys. Soc. 24, 355 (1979); R. H. Baughman, Bull. Am. Phys. Soc. 24, 418 (1979); G. B. Street, Bull. Am. Phys. Soc. 24, 418 (1978).

[8] D. M. Ivory, G. G. Miller, J. M. Sowa, L. W. Shacklette, R. R. Chance, and R. H. Baughman, J. Chem. Phys. 71, 1506 (1979).

[9] R. V. Kasowski and O. K. Andersen, Solid State Commun. 11, 799 (1972); R. V. Kasowski, Phys. Rev. B 14, 3398 (1976).

[10] R. V. Kasowski and E. B. Caruthers, to be published.

[11] R. H. Baughman, S. L. Hsu, G. P. Pez, and A. J. Signorelli, J. Chem. Phys. 68, 5405 (1978).

[12] The structure proposed by R. H. Baughman *et al.*, in Proceedings of the NATO Advanced Study Institute on Molecular Metals, Les Ares, France, 10–16 September, 1978 (to be published), was extrapolated from limited powder-diffraction data on *trans*-$(CH)_x$ and crystal packing of model compounds, such as diphenylpolyenes.

[13] J. C. Slater, Phys. Rev. 81, 385 (1951). We have repeated some of the calculations reported here for $\alpha = 0.7$. This leads to only small changes in the bands. The key overlap between As s levels and C=C π levels remains.

[14] R. V. Kasowski, W. Y. Hsu, and E. B. Caruthers, to be published.

[15] R. E. Peierls, *Quantum Theory of Solids*, Oxford Univ. Press, Oxford, England, 1955), 1st ed., p. 108; M. J. Rice and S. Strassler, Solid State Commun. 13, 125 (1973).

[16] P. M. Grant and I. P. Batra, Solid State Commun. 29, 225 (1979).

[17] M. H. Whangbo, R. Hoffman, and R. B. Woodward, to be published.

[18] T. Yamabe, K. Tanaka, H. Terama-e, K. Fukui, A. Imamura, H. Shirakawa, and S. Ikeda, J. Phys. C 12, L257 (1979).

[19] A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists*, (Wiley, New York, 1961), p. 207.

[20] H. Shirakawa, T. Sasaki, and S. Ikeda, Chem. Lett. 1978, 1113; S. L. Hsu, A. J. Signorelli, G. P. Pez, and R. H. Baughman, J. Chem. Phys. 69, 106 (1978).

[21] N. Bartlett, R. N. Biagioni, B. W. McQuillan, A. S. Robertson, and A. C. Thompson, J. Chem. Soc. Chem. Commun. 1978, 200; N. Bartlett, B. McQuillan, and A. S. Robinson, Mater. Res. Bull. 13, 1259 (1978). Our preliminary calculations show that AsF_6^- contributes holes to the graphite valence band, but does not provide conductivity between widely spaced graphite planes.

[22] A. G. MacDiarmid, private communication.

[23] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. 42, 1698 (1979).

[24] M. J. Rice, Phys. Lett. 71A, 152 (1979).