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Electronic structure of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) and Nb by the pseudofunction energy-band technique

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The pseudofunction energy-band method is a full potential, *ab initio* technique with no adjustable parameters. The basis function is related to the pseudofunction used to create *ab initio* pseudopotentials. Orthogonalization of the pseudofunction to the core states is accomplished as in the augmented plane-wave method (APW) or linear augmented plane-wave method. The applicability of the pseudofunction method to both localized bonding as in molecules or to delocalized bonding as in metals is demonstrated with application to Nb and tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ). The electronic and structural properties calculated for Nb agree well with that of the APW and Korringa-Kohn-Rostoker (KKR) methods. The energy bands obtained from an *ab initio* self-consistent energy-band calculation for TTF-TCNQ are successful in providing new insight into the properties of TTF-TCNQ. The computed optical properties, Fermi surface wave vector, and charge transfer agree quantitatively with experiment for TTF-TCNQ.

I. INTRODUCTION

The pseudofunction (PSF) energy-band method[1] has been previously shown to give energy bands and structural properties for Si,[2] a Si surface,[1] and a CO molecule[1] in good agreement with experiment and other methods. We have also shown that energy bands calculated with the PSF method for the organic superconductor β-$(ET)_2X$ ($X^- = |_3^- \mathrm{Au}|_2^-$, and $|\mathrm{Br}_2^-$) (Ref. 3) agree very well with extended Hückel calculations.[4] The Hückel calculations give a Fermi surface in agreement with experiment.[4] Such comparisons indicate that the PSF method very accurately computes energy bands for systems with strong covalent bonding and large non-muffin-tin potentials. In this paper, the PSF method is used to compute energy bands for Nb, a *d*-band metal, which agree well with those of the Korringa-Kohn-Rostoker (KKR) (Ref. 5) and augmented plane-wave (APW) (Ref. 6) methods. The computed lattice constant and bulk modulus also agree well with experiment. These results thereby show that the PSF method is accurate for *d*-band materials in addition to *s-p* bonded systems reported earlier.[1-3]

Tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) continues to interest the scientific community, because its properties are most unusual for an organic material. The most intriguing property is that it is excellent metal with conductivity similar to that of metals at room temperature.[8,9] A transition to semiconducting behavior occurs at approximately 54 K. TTF-TCNQ was the first organic material to exhibit such interesting behavior. Various proposals have been advanced to explain the metal-insulator behavior. A review of the literature indicates that it is currently thought that the unusual behavior results from charge-density wave phenomena.[8,9] In the metallic region, charge-density waves enable metallic conduction.[10] As the temperature is lowered, the charge-density waves are pinned by impurities and a semiconducting state results. The results of optical conductivity experiments[10] have also been interpreted in terms of the charge-density wave model. In addition to assuming that charge-density waves are optically excited, a pseudogap and strong temperature dependence are also features of that model.

Another point of view is that the metallic properties are a result of a band crossing.[11,12] The metal-insulator transition results from a structural change that splits the bands at the crossing point. This point of view is based on cluster calculations[11] for TTF clusters and TCNQ clusters and on extended Hückel computations.[12]

Because of the complexity of TTF-TCNQ, no *ab initio* self-consistent calculations of its electronic structure have previously been carried out. With the pseudofunction method (PSF),[1] this turns out to be feasible. For the room-temperature crystal structure the band structure is able to account for most of the experimental data in the "metallic" state above 54 K. We find that the TTF and TCNQ bands cross. A charge transfer of 0.68 electrons results which is in very good agreement with the experimental estimate[13] of 0.59 electrons. Computation of the optical conductivity[14] shows a peak at 0.08 eV with a magnitude that decreases by a factor of approximately 2 as the temperature is increased from 50 to 300 K. This is nearly identical to that measured experimentally for the "metallic" state. The energy-band or single-particle picture accounts quantitatively for the optical properties and suggests that there is no pseudogap, contrary to previous interpretations.[10] The optical peak results from a transition between TTF and TCNQ bands in the region where the bands cross and hybridize strongly. The Fermi factor occupation causes this optical-absorption peak to be highly sensitive to temperature as observed experimentally. Finally, neutron and x-ray measurements[15] have measured a Fermi surface wave vector ($2k_F = 0.29b^*$), which is very close to our computed value ($2k_F = 0.31b^*$) where b^* is the wave vector along the stack. Charge-density waves would be necessary as a mechanism for driving such structural transitions.

II. PSF METHOD

The PSF method has been detailed in previous work[1,2,7] and will not be repeated here. For the Nb calculation, the basis set consists of nine *s-p-d* PSF orbitals centered on the Nb atom. The individual PSF orbitals are constructed from a linearized-muffin-tin orbital by replacing the oscillatory behavior within the core region by a smooth function. The PSF orbital resembles the pseudofunction orbital used to construct *ab initio* pseudopotentials.[16] The smoothly varying pseudofunctions are then expanded in 729 (9^3) plane waves. The number of plane waves is obtained from the condition that $|G|_{\max} {}^* R_{\mathrm{mt}} = 7$, where G is a reciprocal-lattice vector and R_{mt} is the muffin-tin radius. The plane waves in the PSF orbitals are then augmented as in the linear augmented plane-wave (LAPW) method[17] to obtain the final basis set. The PSF basis set changes as the potential changes during the iteration to self-consistency, because the potential from which the radial solutions are formed changes. The Hedin-Lundquist exchange-correlation function[18] is used in constructing the potential and total energy. The nonspherical portion of the potential is expanded in 4913 (17^3) plane waves. Nb has a very small nonspherical potential, because it forms in the close-packed bcc crystal structure. The muffin-tin approximation used in the KKR (Ref. 5) and APW (Ref. 6) methods should be appropriate for Nb. It is widely accepted that KKR and APW calculations for Nb are very accurate. The non-muffin-tin region becomes important only if a small muffin-tin radius is used which then makes the interstitial region very large.

The crystal structure of TTF-TCNQ was first determined by Kistenmacher, Phillips, and Cowan.[19] There are parallel segregated stacks of TTF and TCNQ ions that interact weakly with each other. The unit cell contains two molecules of TTF and TCNQ (68 atoms per unit cell). The energy-band computation is unusually difficult because there are many atoms in the unit cell and the distance between neighboring atoms is very small (approximately 1.25 Å). In the PSF method, the nonspherical part of the crystal potential is expanded in plane waves. The short interatomic distances and strong covalency required that the nonspherical potential be expanded in 114 009 plane waves. For a basis set, two sets of sp^3 orbitals were used for all non-H atoms. The H atoms were represented by *s* orbitals. The resultant matrix size is 432 at a general k point.

TABLE I. Structural Properties of Nb.

	Lattice constant	Bulk modulus
Experiment[a]	6.236 a.u.	1.70 Mbar
PSF ($R_{\mathrm{mt}} = 2.1$ a.u.)	6.275 a.u.	1.73 Mbar
PSF ($R_{\mathrm{mt}} = 2.5$ a.u.)	6.200 a.u.	1.72 Mbar
APW	6.160 a.u.	1.95 Mbar
KKR	6.200 a.u.	1.68 Mbar

[a] *American Institute of Physics Handbook,* 3rd ed. (McGraw-Hill, New York, 1970).

III. RESULTS

A. Nb

The total energy was calculated as a function of lattice constant for Nb with Hedin-Lundquist[18] exchange-correlation functions. In Table I, the computed lattice constant and bulk modulus is compared to experiment and the KKR (Ref. 5) and APW (Ref. 20) methods. The agreement with experiment and other calculations is very good. The PSF calculations were performed for two different muffin-tin radii in order to verify that the results are not sensitive to R_{mt}. For a small radius of 2.10 a.u., the non-muffin-tin region becomes very large, and it is important to have the accurate nonspherical potential representation inherent to the PSF method. The PSF results in Table I show the computed physicals are not very sensitive to R_{mt}.

In Table II, the PSF energy bands are compared to

TABLE II. Energy-band comparison with KKR and APW.

	KKR	APW	PSF
Γ_1	−0.41	−0.469	−0.474
Γ_{12}		0.189	0.222
$\Gamma_{25'}$	0.000	0.000	0.000
N_1	−0.296	−0.310	−0.301
$N_{1'}$		0.133	0.152
N_2	−0.151	−0.150	−0.146
N_3		0.433	0.465
N_4		0.249	0.223
$N_{4'}$		0.805	0.776
P_1		0.673	0.542
$P_{3'}$		0.259	0.287
P_4		−0.111	−0.104
H_{12}	−0.325	−0.323	−0.300
$H_{25'}$		0.375	0.403
H_{15}		0.647	0.701

those of the APW (Ref. 6) and KKR (Ref. 5) methods. The agreement for all the bands is very reasonable. Small differences could be due to the details of the calculations such as lattice constant and exchange-correlation potential. Recently, Nicholson and Faulkner[21] compared their quadratic KKR bands with several different methods and found agreement similar to ours.

Thus, the bulk modulus, lattice constant, and energy bands of Nb computed with the pseudofunction method agree well with the KKR and APW methods. Such agreement indicates that the PSF method is accurate for *d*-band materials. The PSF method even works well when a very small muffin-tin radius is chosen which makes the non-muffin-tin region large.

B. TTF-TCNQ

The energy bands for TTF-TCNQ are shown in Fig. 1 for the primary directions in *k* space. The bands are flat in the directions perpendicular to the stack direction b^*. The bands have a metallic crossing in the *b* direction with a transfer of 0.68 electrons. Dotted lines show the band crossing that would have resulted if the interaction between TTF and TCNQ stacks were turned off. The character of the bands are labeled to show clearly the crossing of the bands. The bands are consistent with very anisotropic behavior and could be considered to be one-dimensional-like because of the narrowness in directions perpendicular to the stack direction. The width of the bands of the bands in the perpendicular direction is of the order of phonon energy 0.03 eV.

The TTF and TCNQ bands are mixed strongly only near where they cross at the Fermi energy. This mixing is especially evident in the optical matrix element M_{ij} between band states *i* and *j* for a given *k* point. This matrix element is very small for transitions from TCNQ bands to TTF bands or vice versa when the energy difference between eigenstates exceeds 0.2 eV. Near the band crossing this matrix element becomes large when the TTF and TCNQ bands approach degenercy. The resultant optical conductivity is shown in Fig. 2(a) for polarizations parallel to the *a*, *b*, and *c* directions. The optical conductivity is only strong for the *b* direction. Figure 2(b) (Ref. 10) shows experiment data indicating that the calculations reproduce the correct shape for polarization parallel to

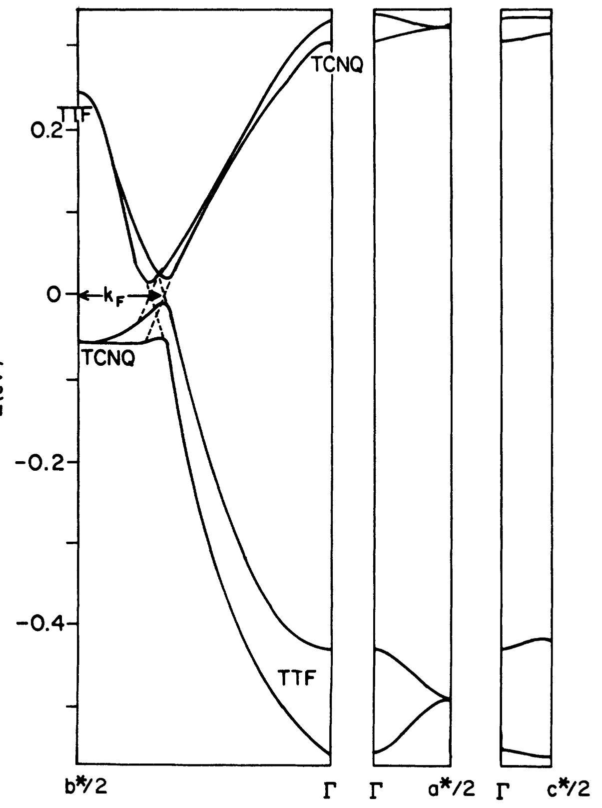

FIG. 1. Energy bands for TTF-TCNQ a^*, b^*, c^* refer to the monoclinic reciprocal space directions *a*,*b*,*c*.

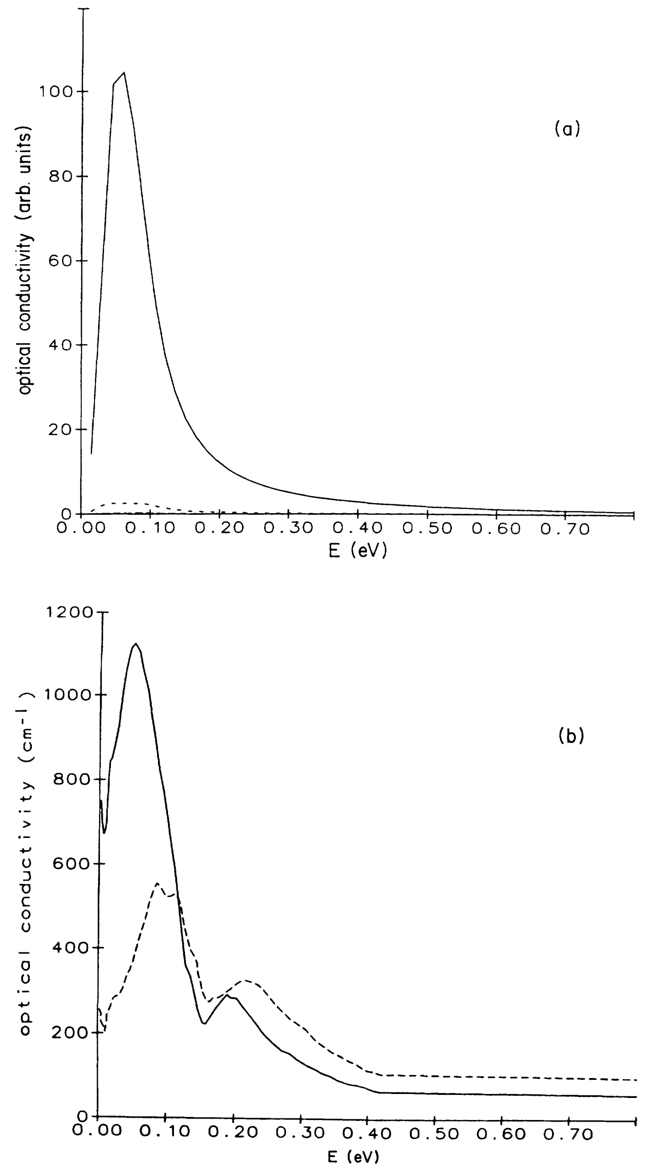

FIG. 2. (a) Computed optical conductivity parallel to *b* (solid), parallel to *a* (dotted), and parallel to *c* (dashed). (b) Measured optical conductivity at room temperature (dashed line) and at 54 K (solid line) (Ref. 10).

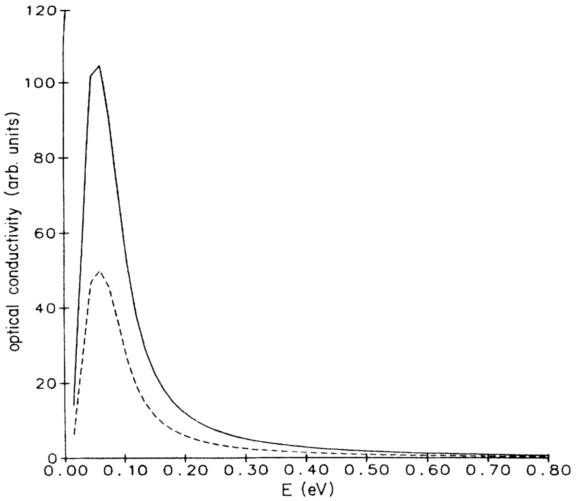

FIG. 3. The computed temperature-dependent optical conductivity for polarization in the b^* direction: solid line for $T=300$ K, dashed for $T=54$ K.

b^*. The peak at zero frequency would be a Drude term due to the metallic electrons resulting from band crossing. The directions perpendicular to b are low magnitude and featureless in agreement with theory.

The optical conductivity has an unusually large temperature dependence. In Fig. 3, the computed optical spectrum is shown for the b^* polarization at temperatures 54 and 300 K. The introduction of the Fermi factor causes the magnitude of the spectra to change in accordance with the temperature dependence obtained experimentally[10] and shown in Fig. 2(b). The shift in peak energy with temperature is probably due to small structural changes. There is also a secondary peak which we cannot account for. We would expect the mixing between the TTF and TCNQ bands to be sensitive to the exact details of the structure as a function of temperature. Even though the peak occurs at around 0.1 eV (1000 K) there is still substantial temperature dependence in this lower temperature range. This occurs because there are actually four different band gaps with the smallest of approximate magnitude 0.02 eV. The optical matrix element is extremely small between the bands separated by the small gaps. Thus even though the electronic population is controlled by the small gap, the optical conductivity is only strong for interband transitions between bands separated by the large gap.

Neutron- and x-ray-scattering studies[15] have independently measured the Fermi wave vector k_F. These measurements cannot determine whether their measured k_F is relative to a hole or electron surface. Our bands in Fig. 1 give a k_F very close to that of experiment.

$$2k_{F\text{theory}}=0.31b^* \quad 2k_{F\text{exp}}=0.29b^* \ .$$

Theory clearly indicates that k_F is relative to the zone edge in the b direction. The charge transfer is also clearly evident from Fig. 1 to be 34% of the TTF band or 0.68 electrons. The estimate from experiment[10] is 0.59 electrons.

The previous theoretical interpretation[10] of the optical conductivity is that the peak in the experimental data near 0.08 eV is due to a collective-mode absorption. The width is due to collective-mode lifetime. A further assumption of the collective-mode behavior is that the $2k_F$ scattering of the electron Bloch waves in the vicinity of k_F leads to pseudogap in the density of states. This gap is reflected in the peak at 0.08 eV in the optical conductivity. Pinning of the CDW by impurities results in an insulator at 54 K. Our *ab initio* energy-band picture is able to account for the optical data via interband transitions and a Drude tail.

Our results for the single-particle states also suggests that previous analytic[22] and numerical[23] many-body calculations meant to model the present system need to be modified. These calculations assume a single-band picture with the electrons interating with a short-range potential. In the renormalization group and the parquet-diagram-type calculations an nth-order perturbation term is proportional to $\mathrm{In}^n(T/E_F)$. In the present case, because the density of states possesses a saddle point, the corresponding factor is proportional to $1/(EG+T/E_F)^n$. While qualitatively the origin of the $4k_F$ and $2k_F$ instability may still be valid, the quantative picture can be different.

Ab initio energy-band theory appears to offer the possibility of greatly improving the understanding of the properties of organic materials. Properties previously attributed to collective effects or to strong electron-electron correlations may be due to single-particle effects as we have shown for TTF-TCNQ. The local-density potential[18] utilized here seems to be a very accurate and computationally viable method for organic materials. The early work on clusters[11,12] are qualitatively in agreement with our results. We have essentially added the interaction between stacks which was missing in the cluster calculations. This allowed our interpretation of a wider set of data than was possible by considering only a cluster.

We have advanced an interpretation of the experimental data based on fully self-consistent full potential-energy-band calculations. TTF-TCNQ is found to have a gap due to band crossing. The gap is so small that metallic behavior is expected at high temperatures. The semiconducting behavior will result as the temperature is lowered and the Fermi factor approaches 1.0. Such behavior can only be averted if the bands are broadened in the direction perpendicular to the stacks by a stronger stack-stack interaction. TTF-TCNQ is thought to be a one-dimensional conductor. However, the band crossing gap and peak in the optical conductivity is a result of interaction or hybridization between the stacks, which is actually a deviation from one-dimensional behavior. If there were no interaction between stacks, the gaps would not exist and the matrix elements giving rise to the low-energy peaks would not occur.

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