PHYSICAL REVIEW B VOLUME 18, NUMBER 12 15 DECEMBER 1978

$(SN)_x$ with hydrogen impurities in the coherent-potential approximation

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(Received 3 February 1978)

A procedure to solve the coherent-potential-approximation (CPA) equation for energy- and k-dependent self-energies is developed. This version makes it possible to apply the CPA method to cases when the density-of-states curves of the constituent systems differ rather strongly. As a first application the density-of-states curves of the valence band of the mixed system consisting of $(SN)_x$ and $(SNH)_x$ linear chains were calculated for hydrogen concentrations between 3 and 50 mole%. The results show a significant effect of the hydrogen impurities on the density of states of $(SN)_x$.

I. INTRODUCTION

Highly conducting polymers like $(SN)_x$ [poly(sulphurnitride)] have raised considerable interest in the last ten years. $(SN)_x$ is a highly anisotropic metal at higher temperatures and becomes superconductive below 0.26 °K.[1] To understand the physical properties of this system a fair knowledge of its electronic structure is needed. Several authors performed, for the one-dimensional $(SN)_x$ chain, semiempirical and approximate (for instance, using simplified atomic potentials) *ab initio* calculations[2] that were followed by two minimal-basis-set *ab-initio* crystal-orbital [self-consistent-field (SCF) linear-combination-of-atomic-orbitals (LCAO) crystal orbital[3] (CO)] calculations.[4] There are also in the literature non-self-consistent orthogonalized-plane-wave (OPW) and LCAO calculations performed for the three-dimensional system.[5] In addition we performed an *ab-initio* double-ζ band-structure calculation for the linear chain,[6] that has given rather good agreement with experiment for the effective electronic mass and the density of states at the Fermi level.

Recently there have been numerous attempts to produce compounds analogous to $(SN)_x$.[7] The modification of $(SN)_x$ by bromine was reported[8] and the properties of $(SN)_x$ reacted with I_2 and ICl are under investigation.[8] In addition, at IBM (San Jose) 5- to 10-mole% hydrogen was found in $(SN)_x$.[9] The position of the hydrogen impurities is unknown, but most probably the H atoms bind to the N atoms. In this way, they change the hybridization state of the N atoms and the number of π electrons in the partially filled band of $(SN)_x$ (in a $-S{=}N-$ unit there are three π electrons while in a $-S-N\text{-}H-$ unit there are four).

To determine theoretically the shift of the Fermi level and the change in the density of states when $(SN)_x$ is modified, we applied the coherent-potential approximation[10] (CPA) to calculate the density of states of the partially filled band of the mixed chain using a newly developed method which does not neglect the k dependence of the self-energy. As a first step the effect of hydrogen impurities or hydrogen doping is investigated because *ab-initio* band structures of the pure $(SN)_x$ and the pure $(SNH)_x$ system[11] as input for the CPA formalism were available. To study the effect of I_2 or Br_2 impurities *ab-initio* band-structure calculations using effective core potentials[12] for the heavy atoms are in progress.

II. METHOD

The CPA equation[10] for a single band is in the single-site approximation

$$\Sigma(k,E)=f\Delta(k)/\{1+[\Sigma(k,E)-\Delta(k)]G_e(E)\}, \tag{1}$$

where f means the percentage of impurities (system B), $0\leq f\leq 1$, and $\Delta(k)=\epsilon^B(k)-\epsilon^A(k)$ (A stands for the reference system). The Green's function for the effective medium $G_e(k,E)$ is defined through the Dyson equation

$$G_e=G^0+G^0\Sigma G_e. \tag{2}$$

Here $G^0(k,E)$ is the Green's function of pure A,

$$G^0(k,E)=[E-\epsilon^A(k)]^{-1}, \tag{3}$$

$$G^0(E)=\Omega^{-1}\sum_k[E-\epsilon^A(k)]^{-1},$$

and therefore

$$G_e(k,E)=[E-\epsilon^A(k)-\Sigma(k,E)]^{-1}. \tag{4}$$

Finally,

$$G_e(E)=\Omega^{-1}\sum_k G_e(k,E)$$

$$=\Omega^{-1}\sum_k[E-\epsilon^A(k)-\Sigma(k,E)]^{-1}. \tag{5}$$

When the k dependence of Σ can be neglected, i.e., the two bands $\epsilon^B(k)$ and $\epsilon^A(k)$ are only shifted to different centers on the energy scale without changing their shapes and Δ is just the k-independent separation, then $G_e(E)$ is simply[13]

$$G_e(E) = G^0(E - \Sigma(E)) . \tag{6}$$

That is, the Green's function for the disordered system is given by that of the unperturbed periodic chain evaluated at the point $z = E - \Sigma(E)$ in the complex plane. The CPA method is usually applied in this form[14] for actual calculations on real systems (e.g., NiCu alloys[13]).

The following expressions define a simple numerical procedure which takes account of the k-dependence of Δ and Σ in the general case.

The spectral density is given by[13]

$$\begin{gathered} A_e(k,E) = -\pi^{-1} \operatorname{Im} G_E(k, E+i0) , \\ \int_{-\infty}^{\infty} A_e(k,E)\, dE = 1 . \end{gathered} \tag{7}$$

The (average) density of states per molecule is then

$$\begin{gathered} \rho_e(E) = \Omega^{-1} \sum_k A_e(k,E) = -\pi^{-1} \operatorname{Im} G_e(E+i0) , \\ \int_{-\infty}^{\infty} \rho_e(E)\, dE = 1 . \end{gathered} \tag{8}$$

Using the Kramers-Kronig relations,[15] one obtains

$$G_e(E) = \int_{-\infty}^{\infty} \frac{\rho_e(E')\, dE'}{E - E'} . \tag{9}$$

With the definition of the division of two complex numbers

$$\frac{\alpha_1 + i\beta_1}{\alpha_2 + i\beta_2} = \frac{\alpha_1\alpha_2 + \beta_1\beta_2}{\alpha_2^2 + \beta_2^2} + i\,\frac{\alpha_2\beta_1 - \alpha_1\beta_2}{\alpha_2^2 + \beta_2^2} , \tag{10}$$

we obtain from (4),

$$\operatorname{Im} G_e(k,E) = \frac{\operatorname{Im}\Sigma(k,E)}{[E - \epsilon^A(k) - \operatorname{Re}\Sigma(k,E)]^2 + [\operatorname{Im}\Sigma(k,E)]^2} \tag{11}$$

(which is a resonance formula of the asymmetric Breit-Wigner type).

To obtain suitable starting values for $\Sigma(k,E)$ and $G_e(E)$ one takes for $f \ll 1$, $\Sigma^{(0)} = 0$ and

$$G_e^{(0)}(E) = G^0(E) = \int_{-\infty}^{\infty} \frac{\rho_0(E')\, dE'}{E - E'}$$

[$\rho^0(E')$ is the density of states of pure system A]. For larger f's one starts from the virtual-crystal approximation: $\Sigma^{(0)} = f\Delta(k)$ and

$$G_e^{(0)}(E) = \int_{-\infty}^{\infty} \frac{\rho_{\rm vc}(E')\, dE'}{E - E'} ,$$

where $\rho_{\rm vc}(E')$ is the density of states belonging to the energy band $E_{\rm vc}(k) = (1-f)\epsilon^A(k) + f\epsilon^B(k)$. $\rho^0(E')$ and $\rho_{\rm vc}(E')$ were calculated by the method of Delhalle,[16] while for the determination of $G_e^{(0)}(E)$ the procedure of Kirkpatrick *et al.*[13] was used.

Solving Eq. (1) with these guesses, one obtains complex values of $\Sigma^{(1)}(k,E)$ for every E and k [$\Sigma^{(0)}$ is real, but $G_e^{(0)}(E)$ is complex] and can then start the iteration procedure. Substituting into Eq. (11) and using Eqs. (7)–(9) one obtains new values for $G_e(E)$. This procedure is repeated until self-consistency is reached. Our SCF criterion was

$$\max_{\{i\}} \left| \rho_e^{(n)}(E_i) - \rho_e^{(n-1)}(E_i) \right| \leq 10^{-3}\ (\text{a.u. mole})^{-1} . \tag{12}$$

To reach self-consistency between 24 ($f = 0.3$) and 70 ($f = 0.5$) iteration steps were needed. The corresponding computing times on a CYBER 172 were 100 and 200 sec, respectively.

For the case treated in this paper the other details of the numerical procedure are the following: (i) In building up a mesh for the energy range in which the density of states is calculated the mesh points were not chosen equidistantly but were made more dense in the range of $\rho^B(E) \neq 0$ and in regions with narrow peaks. Finally we choose 93 points in the energy range of about 10 eV and the same number of k points $(0 \leq k_i \leq \pi/a)$ for which $\Sigma(k,E)$ was calculated in every iteration step. The corresponding 93 points of $\Delta(k)$ were calculated by means of a parabolic interpolation fit of the nine points of the $\epsilon^A(k)$ and $\epsilon^B(k)$ curves. (ii) The starting values for $\Sigma(k,E)$ were calculated with the virtual-crystal values for $\Sigma^{(0)}$ and $G_e^{(0)}(E)$, as mentioned above. These starting values yielded faster convergency than the other guesses obtained with $\Sigma^{(0)} = 0$ and $G_e^{(0)} = G^0$. (iii) For $f\Delta(k) \approx 0$, $\Sigma(k,E) \approx 0$, and therefore, from (11), and taking into account the relation

$$\delta(x) = \lim_{\alpha \to 0} \frac{1}{\pi} \frac{\alpha}{x^2 + \alpha^2} , \tag{13}$$

one obtains sharp δ peaks in the spectral density (7). To handle this for discrete E_i points in the numerical integration we used the normalization condition for A_e in (7) in every iteration step. The procedure was checked with $f = 10^{-5}$ for which the spectral density shows practically the δ structure of pure system A.

It was checked by numerical integration that the total area under the curves in Figs. 1–3 is 2.0, thus leading to the proper number of electrons per unit cell for a single band (taking into account both spin directions). Since in pure (SN)$_x$ the valence band is only half occupied (one electron per unit cell in the valence band), the position of the Fermi level ϵ_F was then determined by numerical inte-

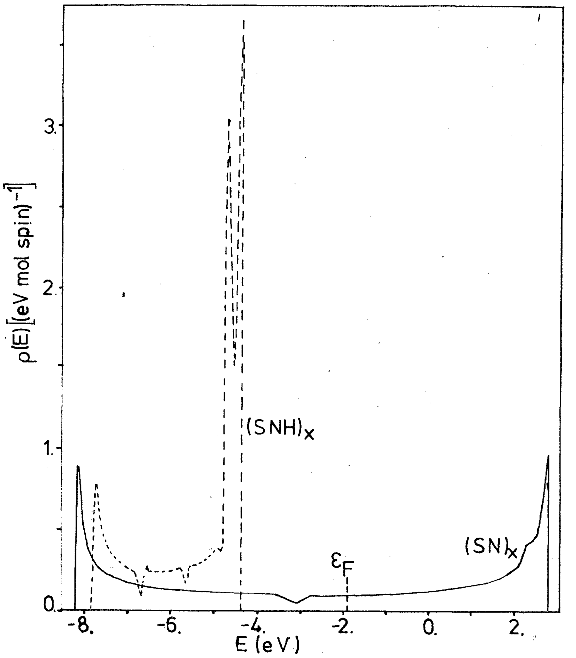

FIG. 1. Density-of-states curves of the pure $(SN)_x$ and $(SNH)_x$ systems [in (eV mole spin)$^{-1}$ units].

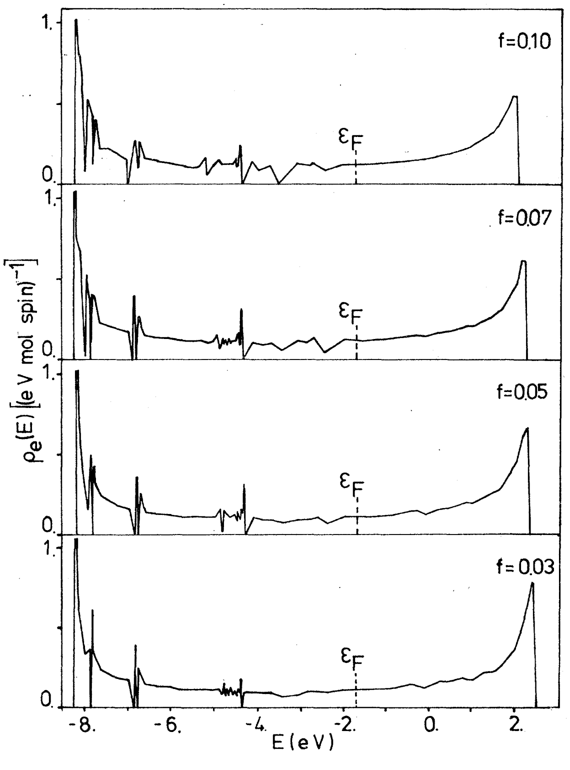

FIG. 2. Density-of-states curves of the $(SN)_x$ and $(SNH)_x$ mixed system obtained in the CPA with $f = 0.03$, 0.05, 0.07, and 0.10 [in (eV mole spin)$^{-1}$ units].

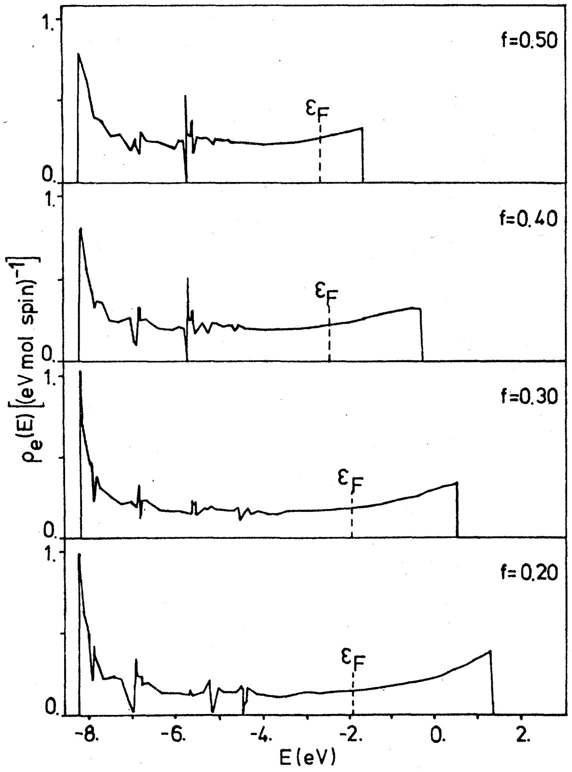

FIG. 3. Density-of-states curves of the $(SN)_x$ and $(SNH)_x$ mixed system obtained in the CPA with $f = 0.2$, 0.3, 0.4, and 0.5 [in (eV mole spin)$^{-1}$ units].

gration from

$$\int_{\epsilon_{\min}}^{\epsilon_F} \rho_e(E)\,dE = 1+f . \tag{14}$$

To determine $\Delta(k)$ we performed a minimal basis[17] SCF LCAO CO calculation for the pure $(SN)_x$ (system A) and for the pure $(SNH)_x$ (system B).[11] For f we took values between 0.03 and 0.1 and between 0.2 and 0.5 [to see the effect of possible hydrogen doping of $(SN)_x$].

III. RESULTS

In Fig. 1 we give the density of states curve of the partially filled band of $(SN)_x$ and of the valence band of $(SNH)_x$. In Figs. 2 and 3 we show the density of states curves of the mixed systems obtained with our method using, respectively, $f = 0.03$, 0.05, 0.07, and 0.10 and 0.20, 0.30, 0.40, and 0.50.

IV. DISCUSSION

The most surprising result is the complicated structure of the impurity band with spikes and dips where the density of states goes to zero. This structure is well known from computer experiments for linear chains[18] and from cluster-

CPA calculations,[19] but could not be obtained with the simple CPA using a k-independent Σ. To exclude a numerical effect we changed the number and position of the mesh points both for E and k independently, we chose a denser mesh at the points where $\rho_e(E)=0$, we tried to damp out the oscillations in the first iteration steps. For $f \geq 10^{-2}$, however, these spikes and dips reoccured always when self-consistency was reached. Our method therefore seems to be a simple and fast way to overcome the nonphysical features of the usual CPA such as a k-independent self-energy and an impurity band with no structure.

From Fig. 1 one can see that the $(SNH)_x$ periodic chain has, as one expects, a much narrower valence band than $(SN)_x$ (with corresponding large peaks in the density of states).[20] The Fermi level of $(SN)_x$ lies at -1.90 eV, while the upper limit of the completely filled valence band of $(SNH)_x$ is at -4.38 eV. One would expect on the basis of the rather large differences in the density of states curves of the two systems that in the mixed system even a small percentage of $(SNH)_x$ would have a comparatively large influence on the density of states curve of pure $(SN)_x$.

This expectation is fulfilled as one can see from Fig. 2 where the density-of-states curves obtained in the CPA approximation for the mixed system with 10% (or less) hydrogen are shown. Even at very low hydrogen concentration ($f=0.03$) new peaks in the density of states curve start to develop in the region between -4.4 and -8.0 eV. At higher f values (see Fig. 3) peaks of $(SN)_x$ and $(SNH)_x$ in the region between -7 and -8 eV fuse to one broader peak. On the other hand due to the very high but extremely narrow peaks of $(SNH)_x$ between -4.8 and -4.4 eV new peaks develop but are shifted to the region around -5.6 eV (see especially the curve belonging to $f=0.50$). In this case one sees clearly demonstrated the fact that the CPA method (especially at higher impurity concentration) gives essentially different results than the simple virtual crystal approximation.

The position of the Fermi level of the mixed system is not a sensitive function of f at low concentrations ($\epsilon_F=-1.9$ eV for $f=0.00$, $\epsilon_F=-1.6$ eV for $0.03 \leq f \leq 0.1$, $\epsilon_F=-1.9$ eV for $f=0.2$). At higher concentrations, of course, its position shifts towards lower energies ($\epsilon_F=-2.6$ eV at $f=0.50$). The density of states at the Fermi level increases monotonically with increase of $f[\rho_e(\epsilon_F)=0.10$, 0.12, 0.13, 0.18, and 0.26 at $f=0.00$, 0.05, 0.10, 0.30, and 0.50, respectively].

The very narrow spikes and dips in the density of states due to the hydrogen impurities as calculated with our method could be, in principle, detected by ultraviolet-photoemission spectroscopy (UPS) or x-ray-photoelectron spectroscopy (XPS). However, due to a combination of the poor XPS resolution and incomplete knowledge of exactly how to treat the background corrections near ϵ_F [known from the XPS determination of the valence band structure of $(SN)_x$],[21] it is not certain if such experimental measurements would show the structure in the valence band. On the other hand, if such narrow peaks were found in XPS data, they probably could be attributed to hydrogen impurities as our calculations show.

According to the BCS theory the superconductivity transition temperature T_c depends exponentially on the electronic density of states at the Fermi level[22]

$$T_c = 1.14\Theta_D \exp(-1/\rho(\epsilon_F)V)\,, \tag{15}$$

where Θ_D is the Debye temperature and V is the effective BCS electron-electron interaction parameter which can be estimated from measurements of the electric resistivity. Early experiments using alloys of molybdenium and niobium[23] over the whole concentration range from pure Nb to pure Mo showed that T_c varies by a factor of over 500, whereas the electron-phonon coupling constant $\rho(\epsilon_F)V$ changes only by a factor of less than 2.

Therefore, assuming an approximate constancy of V over the concentration range[22,23] (or estimating it from electric resistivity data), the densities of states and the positions of the Fermi level calculated for different concentrations and different impurities (H, Br_2, I_2, ICl) can give important indications of the variations of T_c. Furthermore, they can provide information about internal processes such as charge transfer from, or to, the impurities and (if the calculations are done for different model geometries) in combination with experimental data for T_c—about the geometrical arrangement of a certain type of impurity.

In addition, the determination of the electron-phonon coupling constant $\rho(\epsilon_F)V$ can help to clear up the question if changes in the dc conductivity σ_{dc} (and in the related dc scattering lifetime τ_{dc}) due to impurities are dominated by electron-electron scattering of by electron-phonon scattering[8] processes.

ACKNOWLEDGMENTS

We would like to express our gratitude to Dr. S. Suhai for performing the band-structure calculations of the periodic $(SN)_x$ and $(SNH)_x$ chains and to Dr. R. D. Singh for writing a program for the calculation of the density of states of the pure periodic chains. The financial support of the Deutsche Forschungsgemeinschaft (Project No. La 371/1) is gratefully acknowledged.

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[1] For a review, see H. P. Geserich and L. Pintschovius, Adv. Solid State Phys. 16, 65 (1976).

[2] H. Kamimura, A. J. Grant, F. Levy, A. D. Yoffe, and C. D. Pitt, Solid State Commun. 17, 49 (1975); D. E. Parry and J. M. Thomas, J. Phys. C 3, L45 (1975); A. Zunger, J. Chem. Phys. 63, 4854 (1975); S. Suhai and M. Kertész, J. Phys. C 9, L347 (1976); V. T. Rajan and L. M. Falicov, Phys. Rev. B 12, 1240 (1975).

[3] G. Del Re, J. Ladik, and G. Biczó, Phys. Rev. 155, 997 (1967).

[4] C. Merkel and J. Ladik, Phys. Lett. A 56, 395 (1976); M. Kertész, J. Koller, A. Ažman, and S. Suhai, *ibid.* 55, 107 (1975).

[5] W. E. Rudge and P. M. Grant, Phys. Rev. Lett. 35, 1799 (1975); W. Y. Ching, J. G. Harrison, and C. C. Lin, Phys. Rev. B 15, 5975 (1977); I. P. Batra, S. Ciraci, and W. E. Rudge, *ibid.* 15, 5858 (1977).

[6] S. Suhai and J. Ladik, Solid State Commun. 22, 227 (1977).

[7] Recent reviews are Ref. 1 and G. B. Street and R. L. Greene, IBM J. Res. Devel. 21, 99 (1977).

[8] W. D. Gill, W. Bludau, R. H. Geiss, P. M. Grant, R. L. Greene, J. J. Mayerle, and G. B. Street, Phys. Rev. Lett. 38, 1305 (1977).

[9] B. Györffy and S. Faulkner (personal communication).

[10] See, for instance, R. J. Elliott, J. A. Krumhansl, and P. L. Leath, Rev. Mod. Phys. 46, 465 (1974); F. Martino, in *Quantum Theory of Polymers* (edited by J.-M. André, J. Delhalle, and J. Ladik (Reidel, Dordrecht-Boston, 1978).

[11] S. Suhai (unpublished results).

[12] L. R. Kahn, P. Baybutt, and D. G. Truhlar, J. Chem. Phys. 65, 3826 (1976).

[13] S. Kirkpatrick, B. Velický, and H. Ehrenreich, Phys. Rev. B 1, 3250 (1970).

[14] Only in the case of liquid mercury [F. Yonezawa and F. Martino, J. Phys. F 6, 739 (1976)] the k dependence of Σ is maintained (even in the multiband case) but in this work (see Yonezawa and Martino) spherically symmetric atomic potentials and other model parameters were assumed so that the integrals could be evaluated analytically. This formalism, is however, not applicable in the general case.

[15] J. Callaway, *Quantum Theory of the Solid State* (Academic, New York–London, 1974), p. 517.

[16] J. Delhalle, Bull. Soc. Chim. Belges 84, 135 (1975).

[17] W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys. 51, 2657 (1969).

[18] For a review, see R. Dean, Rev. Mod. Phys. 44, 127 (1972).

[19] W. H. Butler, Phys. Rev. B 8, 4499 (1973).

[20] According to our previous double-ζ *ab-initio* band-structure calculation of $(SN)_x$ (Ref. 6) the partially filled band has only a width of 4.1 eV in contrast to the 10-eV width obtained in the minimal basis set calculation presented here. One would expect therefore that in the case of a double-ζ basis set calculation the width of the two chains would not be so different though most probably $(SN)_x$ will have also in this case a larger width.

[21] P. Mengel, P. M. Grant, W. E. Rudge, B. H. Schechtmann, and D. W. Rice, Phys. Rev. Lett. 35, 1803 (1975).

[22] G. Rickayzen, *Theory of Superconductivity* (Interscience-Wiley, New York, 1965).

[23] R. A. Hein, J. W. Gibson, and R. D. Blaugher, Rev. Mod. Phys. 36, 149 (1964).