ELECTRIC CONDUCTION IN n-TYPE GERMANIUM AND CADMIUM SULFIDE

A. FERREIRA da SILVA, I.C. da CUNHA LIMA and M. FABBRI
Instituto de Pesquisas Espaciais – INPE,
Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPq,
12200 São José dos Campos, SP, Brazil

Received 15 December 1980
Revised manuscript received 3 May 1981

The impurity conduction of n-type Ge and CdS is calculated via a previously developed theory for impurity bands in doped semiconductors. Rough agreement with experimental data over a wide range of impurity concentration is found. The comparison with AMO–MT calculation shows a large enhancement due to a stronger electron correlation.

In doped semiconductors (of n-type) three different regions appear in impurity conduction, as quoted by Fritzsche [1]: the low-concentration region ($<10^{16}$ cm^{-3} in Ge) where the conduction is due to electron hopping between impurities (compensation is essential for conduction), the intermediate-concentration region where an activation energy for conduction is observed and the high-concentration region ($>10^{18}$ cm^{-3} in Ge) where the impurity level spreads into an impurity band overlapping the host conduction band, and the conduction is metallic. Many experiments [2–5] have confirmed such classification as the general property of doped semiconductors. These experiments as well as theoretical investigations [6] suggest that the Mott–Hubbard–Anderson (MHA) model [7], in which electron correlation and Anderson localization play the most essential roles, provides a proper description of the novel behavior of doped semiconductors. Matsubara and Toyozawa [8], who will henceforth be referred to as MT, carried out one of the earliest studies along the line of the MHA scheme. They have treated only the random distribution of impurities by the Green's-function technique, but neglected the correlation between electrons. Recent improvements on the MT scheme have been done [9] by incorporating the alternant-molecular-orbital (AMO) method [10] in order to introduce the correlation effects. The comparison of their calculation [11–13] with the measured resistivities is very encouraging.

Here we apply the previously developed theory [14] of MT, which, by use of a Heitler–London (HL) two-particle wave function, takes into account the correlation effects. The calculated resistivities (instead of conductivities, for convenience) of Ge:Sb, Ge:As, CdS:Cl and CdS:In, at zero temperature, show rough agreement when compared to the experimental data over a wide range of impurity concentrations at low temperature (1.7–4.2 K). The results of the AMO–MT calculations are also shown for comparison.

For the sake of simplicity we will briefly outline the HL–MT scheme, while the reader should refer to the original works for details. The original MT scheme for doped semiconductors starts from a tight-binding hamiltonian,

$$H = \sum_i E_i a_i^+ a_i + \sum_{i \neq j} V(R_{ij}) a_i^+ a_j \qquad (1)$$

for a single impurity band, where a_i^+ and a_i are the creation and annihilation operators respectively of an electron

0 031–9163/81/0000–0000/$ 02.50

at the ith impurity site. The site energy values E_i can be assumed to be independent of i [‡1]. As measured from the host conduction band, this can be taken as $-\epsilon_I$, the ionisation energy of an isolated impurity. Here we take this as our energy origin. One assumes no compensation in order to make $E_i = 0$ [or $V_{ii} \equiv V(R_{ii}) = 0$] for all sites. Assuming compensation, we must take into account the diagonal part $\Sigma_i E_i a_i^\dagger a_i$, where E_i differ from site to site [15]; the charged minority gives rise to a spatially fluctuating potential. The $V(R_{ij})(\equiv V_{ij})$ is the integral for the transfer of an electron from the ith site to the jth site:

$$V_{ij} = \int \phi(r - R_j) \frac{-1}{|r - R_i|} \phi(r - R_j)\, \mathrm{d}r = -V_0(1 + \alpha R_{ij}) \exp(-\alpha R_{ij}), \tag{2}$$

calculated by using the hydrogenic 1s state wave function, with V_0 equal to twice the ionisation energy and $1/\alpha$ is the radius of the 1s orbit,

$$\phi(r - R_i) = (\alpha^3/\pi)^{1/2} \exp(-\alpha|r - R_i|). \tag{3}$$

The Green's functions defined by

$$G_{mn}^{(\pm)}(E) = \langle 0|a_m \frac{1}{E - H \pm \mathrm{i}\epsilon} a_n^\dagger|0\rangle, \quad G_{mn}(E) = (2\pi)^{-1}\mathrm{i}\,[G_{mn}^{(+)}(E) - G_{mn}^{(-)}(E)], \tag{4,5}$$

enable us to calculate the dc conductivity. (They are calculated from (1) with configuration averaging over the random distribution of impurities.) Defining

$$\xi^{(\pm)} = Z_\pm \overline{G_{mm}^{(\pm)}(E)}, \tag{6}$$

where the bar means configuration averaging and $Z_\pm = E \pm \mathrm{i}\epsilon$, then $\xi^{(\pm)}$ satisfies the equation

$$1 - \frac{1}{\xi^{(\pm)}} = \frac{N\xi^{(\pm)}}{8\pi^3 Z_\pm^2} \int \frac{v(k)^2 \mathrm{d}k}{1 - (N\xi^{(\pm)}/Z_\pm)v(k)}, \tag{7}$$

where $v(k)$ is the Fourier transform of $V(R_{ij})$.

The dc conductivity is calculated by making use of the Greenwood–Kubo [16] equation

$$\sigma = \lim_{s \to 0^+} \int_0^\infty \mathrm{d}t \int_0^\beta \mathrm{d}\lambda \exp(-st) \langle J(-\mathrm{i}h\lambda) J(t) \rangle, \tag{8}$$

where $\beta = 1/k_B T$, k_B is the Boltzmann constant, $\langle\ \rangle$ means the quantum statistical average under no external field, and $J(t)$ is the Heisenberg representation of the electric-current operator J. By decoupling the current–current Green's function into a sum of products of one-electron Green's functions connecting impurity sites, evaluated at the Fermi energy E_F, one gets

$$\sigma = \frac{2\pi e^2}{3h} \int \Xi(E)[-\mathrm{d}f(E)/\mathrm{d}E]\, \mathrm{d}E, \tag{9}$$

where $f(E)$ is the Fermi distribution function, and

[‡1] The magnitude of V_{ij}(HL) is reduced, $|V_{ij}(\mathrm{HL})| < |V_{ij}(\mathrm{AMO})| < |V_{ij}(\mathrm{MT})|$. The electron correlation substantially reduces the bandwidth via the cut-off of the long-range hopping. V_{ii} does not deviate much from $\epsilon_I = -0.5$ and $V_{ii} \to \epsilon_I$ as $R_{ij} \to \infty$. Therefore it is not unreasonable to assume V_{ii} constant if the doped semiconductors are uncompensated. For further discussion see ref. [20].

$$\Xi(E) = \frac{1}{32\pi^5} \int \left[\frac{1}{v(k)} \frac{\mathrm{d}v(k)}{\mathrm{d}k}\right]^2 \left[2\,\mathrm{Im}\left(\frac{N\xi^{(+)}}{N\xi^{+} - Z_{+}v(k)^{-1}}\right)\right]^2 \mathrm{d}k$$

$$- \frac{1}{4\pi^2} \int R^2 V(R_{ij})^2 \left[\frac{1}{4\pi^2} \int \exp(\mathrm{i}k\cdot R)\,\mathrm{Im}\left(\frac{\xi^{(+)}}{Z_{+}} \frac{N\xi^{+}}{N\xi^{+} - Z_{+}v(k)^{-1}}\right) \mathrm{d}k\right]^2 \mathrm{d}R\,. \tag{10}$$

The Fermi energy is determined by numerical integration from

$$2 \int_{-\infty}^{E_F} D(E)\,\mathrm{d}E = N, \tag{11}$$

where $D(E)$ is the density of states obtained from (4)–(7).

The hamiltonian, which describes the single impurity band, has the same structure as the MT hamiltonian if V_{ij} is defined as the effective hopping integral and $\epsilon_1(V_{ii})$ as the effective value of the diagonal matrix elements of H.

We will calculate the V_{ij} using a Heitler–London two-particle wave function. Therefore, let us consider a pair of neutral impurities located at R_i and R_j forming an H_2-like "impurity molecule". Labelling r_1 and r_2 as the coordinates of the two electrons, the wave function of the impurity molecule is written as

$$\psi(ij; r_1 r_2) = [2(1+S)]^{-1/2}[\phi(r_1 - R_i)\phi(r_2 - R_j) + \phi(r_1 - R_j)\phi(r_2 - R_i)]\,, \tag{12}$$

where $S = \langle\phi(r - R_i)|\phi(r - R_j)\rangle$ is the overlap integral. The energy $E(\alpha, R_{ij}) = \langle\psi(ij; r_1 r_2)|H|\psi(ij; r_1 r_2)\rangle$, where H is the hamiltonian of the impurity molecule, can be calculated analytically in terms of the Slater [17] integrals S, K, J, J' and K':

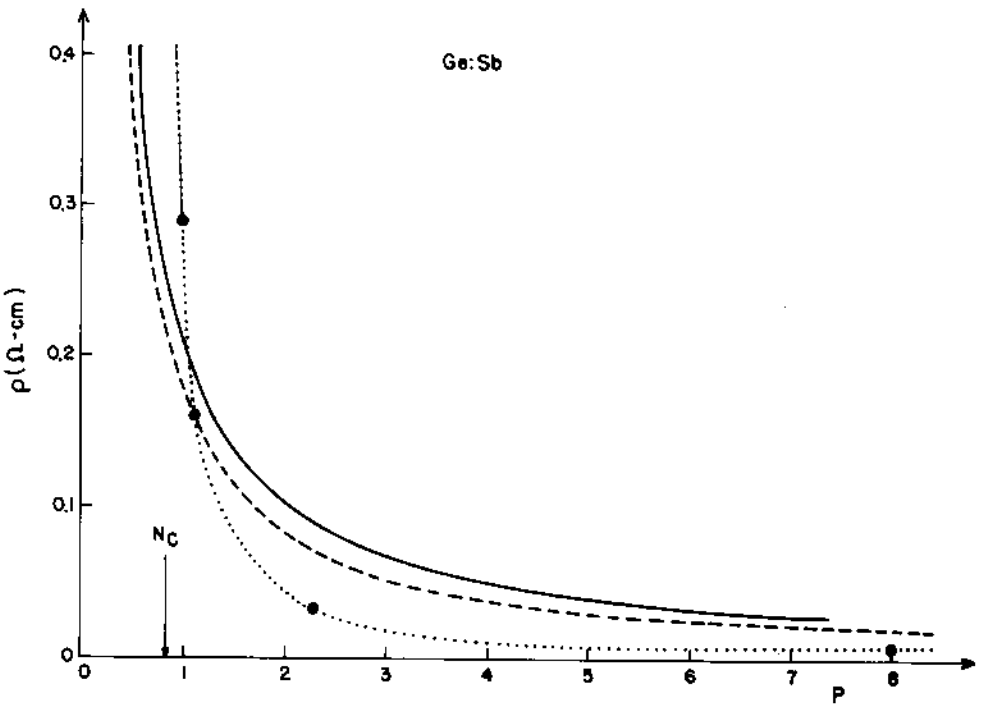

Fig. 1. Theoretical and experimental resistivities as a function of the impurity concentration P for Ge:Sb. Full circles, experiment at 2.5 K; dashed line, AMO–MT calculation; full line, present calculation, both carried out at 0 K. N_C indicates the experimental critical impurity concentration for the MNM transition.

$$E(\alpha, R_{ij}) = [2(1+S^2)]^{-1}[2\alpha^2(1-KS-S^2)+\alpha(J'+K'+4KS+2J-4)+R_{ij}^{-1}]\,, \tag{13}$$

where K' represents the exchange effects and J' represents the electron correlation effect. The optimum values obtained for α when we minimise the ground-state energy (13) are introduced in V_{ij} as well as in V_{ii}. Since we assume V_{ii} to be constant, in order to keep the MT scheme unaltered, our interest here shall only be in the V_{ij}.

To incorporate the HL into the one-electron hamiltonian (1), we have to single out the hopping of only the first electron in the combined field of impurity ions and the second electron. Consequently, we will introduce an effective one-electron hamiltonian $\tilde{H}(r)$ as

$$[\phi(r_1-R_i)+\phi(r_1-R_j)]\tilde{H}(r_1)[\phi(r_1-R_i)+\phi(r_1-R_j)] = \int \psi(ij;r_1r_2)(H-R_{ij}^{-1})\psi(ij;r_1r_2)\mathrm{d}r_2\,. \tag{14}$$

The effective one-electron matrix elements can be written as

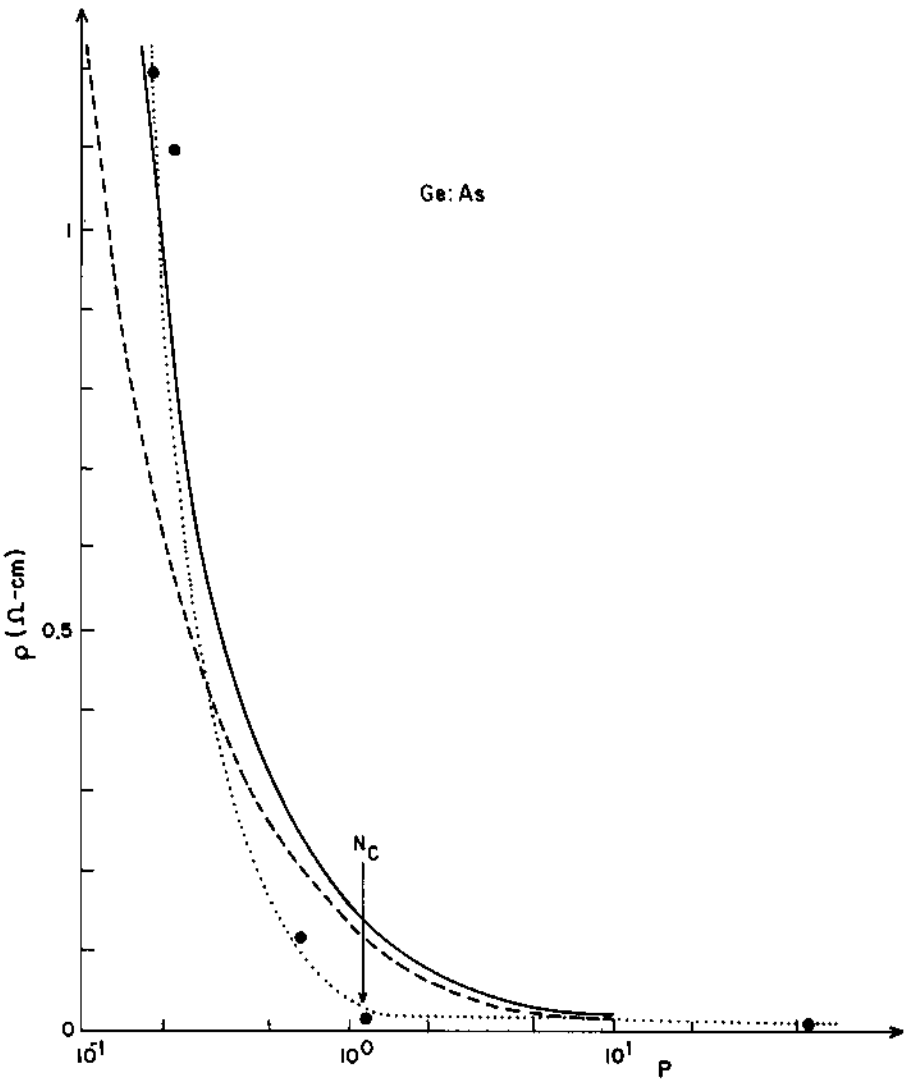

Fig. 2. Same as fig. 1 for Ge:As. Experiment at 4.2 K.

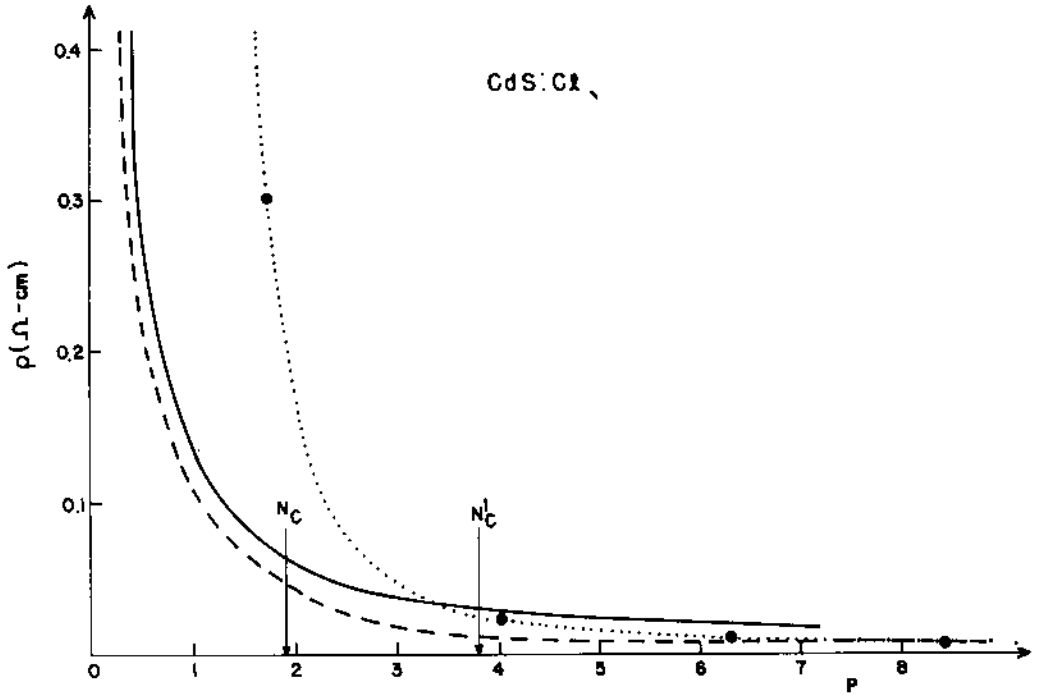

Fig. 3. Same as fig. 1 for CdS:Cl. Experiment at 4.2 K.

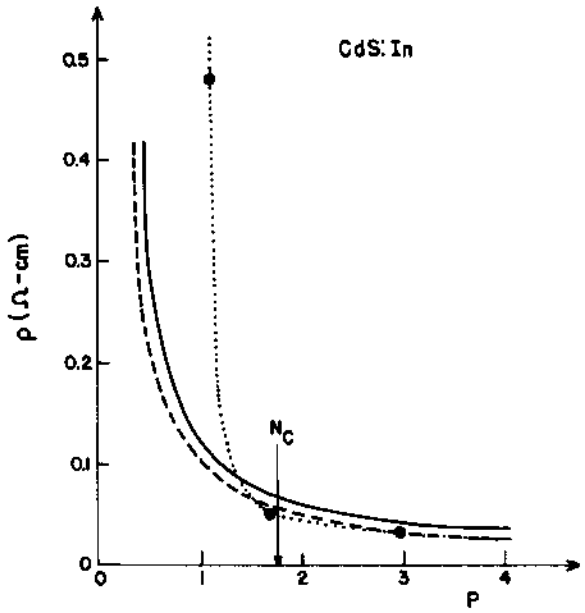

Fig. 4. Same as fig. 1 for CdS:In. Experiment at 1.7 K.

$$V_{ij} = \int \phi(r - R_i)\tilde{H}(r)\phi(r - R_j)\,dr\,; \tag{15}$$

we get for $i \neq j$ the off-diagonal matrix elements

$$V_{ij} = [2(1 + S^2)]^{-1}[\alpha^2(KS + S^2) + \alpha(2KS + \tfrac{1}{2}K')]\,. \tag{16}$$

The calculated resistivities for Ge:Sb, Ge:As, CdS:Cl and CdS:In are plotted in figs. 1 to 4, as functions of the normalized impurity concentration $P = 32\pi N a_H^{*3}$, where a_H^* is the Bohr radius obtained from the experimental ionisation energy [18]. The full lines correspond to the present calculation. The dashed lines correspond to the AMO–MT calculation and the dotted lines with solid circles are the experimental data. The experimental critical impurity concentration N_c (or P_c) for the metal–nonmetal (MNM) transition is indicated with an arrow. For Ge:Sb, $N_c = 0.95 \times 10^{17}$ cm^{-3} or $P_c = 0.8$, $a_H^* = 43.7$ Å [19], the experimental data are from ref. [1] and the AMO–MT theory from ref. [11]; for Ge:As, $N_c = 3.5 \times 10^{17}$ cm^{-3} or $P_c = 1.12$, $a_H^* = 31.7$ Å, experimental data from ref. [4] and theory from ref. [12]; for CdS:Cl, $N_c = 9.0 \times 10^{17}$ cm^{-3} or $P_c = 1.9$ [18], $N_c' = 2.0 \times 10^{18}$ cm^{-3} or $P_c' = 3.8$ [3], $a_H^* = 26.7$ Å, experimental data from ref. [3] and theory from ref. [11]; for CdS:In, $N_c = 10 \times 10^{18}$ cm^{-3} or $P_c = 1.77$, $a_H^* = 26$ Å, experimental data from ref. [5] and theory from ref. [13]. It is worthwhile to point out that the present calculation has shown how sensitive the resistivity is, in n-type doped semiconductors, to changes in the electron correlation, presenting a satisfactory agreement between our calculation and experiment over a wide range of impurity concentrations. Due to the configurational averages of products of two Green's functions treated over the dc conductivity in the original MT scheme, our scheme is only valid for $P > 1$ [8,12]. Uncompensated n-type semiconductors are assumed. We also have to mention that there is no criterion here to determine when the Anderson transition takes place. However, to incorporate the Anderson localization into the present model is really a difficult task.

[1] H. Fritzsche, J. Phys. Chem. Solids 6 (1958) 69.
[2] E.A. Davis and W.D. Compton, Phys. Rev. 140 (1965) A2183;
C. Yamanouchi, K. Mizuguchi and W. Sasaki, J. Phys. Soc. Japan 22 (1967) 859;
Y. Otsuka, S. Ikihata, S. Kobayashi and W. Sasaki, Solid State Commun. 20 (1976) 441.
[3] S. Toyotomi and K. Morigaki, J. Phys. Soc. Japan 25 (1968) 807.
[4] V.G.I. Deshmukh and D.P. Tunstall, J. Phys. 37 (1976) C4-329.
[5] S. Geschwind et al., Proc. Intern. Conf. on Impurity bands in semiconductors (Würzburg, 1979) p. 557.
[6] Y. Ishida and F. Yonezawa, Prog. Theor. Phys. 49 (1973) 731;
H. Aoki and H. Kamimura, J. Phys. Soc. Japan 40 (1976) 6.
[7] N.F. Mott, Metal–insulator transition (Taylor and Francis, London, 1974);
J. Hubbard, Proc. R. Soc. London A276 (1963) 238, A281 (1964) 401;
P.W. Anderson, Phys. Rev. 109 (1958) 1492.
[8] T. Matsubara and Y. Toyozawa, Prog. Theor. Phys. 26 (1961) 739.
[9] K.A. Chao, F.A. Oliveira and N. Majlis, Solid State Commun. 21 (1977) 845;
R. Osorio, N. Majlis and K.A. Chao, J. Phys. C11 (1978) 2779;
K.A. Chao and A. Ferreira da Silva, Phys. Rev. B19 (1979) 4125.
[10] P.O. Löwdin, Phys. Rev. 97 (1955) 1509;
R. Pauncz, Alternant molecular orbital (Saunders, Philadelphia, 1967).
[11] K.A. Chao and A. Ferreira da Silva, J. Phys. C11 (1978) 3661.
[12] K.A. Chao and A. Ferreira da Silva, Int. J. Quantum Chem. Symp. 12 (1978) 461.
[13] A. Ferreira da Silva, J. Phys. C13 (1980) L427.
[14] M. Fabbri, I.C. da Cunha Lima and A. Ferreira da Silva, J. Phys. C, submitted.
[15] K.A. Chao and A. Ferreira da Silva, Phys. Stat. Sol. B90 (1978) K153;
A. Ferreira da Silva, Ph.D. Thesis, University of Linköping, Sweden (1979);
A. Ferreira da Silva, R. Riklund and K.A. Chao, Prog. Theor. Phys. 62 (1979) 584.
[16] R. Kubo, J. Phys. Soc. Japan 12 (1957) 570;
D.A. Greenwood, Proc. Phys. Soc. London 71 (1958) 585.
[17] J.C. Slater, Quantum theory of matter, 2nd Ed. (McGraw-Hill, New York, 1968) p. 417.
[18] P.P. Edwards and J.M. Sienko, Phys. Rev. B17 (1978) 2575.
[19] K.F. Berggren and B. Sernelius, Solid State Commun. 19 (1976) 487.
[20] K.A. Chao and A. Ferreira da Silva, Phys. Stat. Sol. B90 (1978) K153; Phys. Rev. B19 (1979) 4125.