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VARIATIONAL CALCULATIONS OF THE SPIN POLARIZATION INDUCED BY A LOCAL MOMENT IN s-d HYBRIDIZED METALS*

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INTRODUCTION

The problem of the spin polarization induced by a f moment with particular emphasis to s-d mixing effects and d-d correlations in transition metal like hosts has been subject of several calculation [1], [2], [3]. The main feature of this previous work was, keeping the same type of description

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for the s-d hybridized bands [4], to systematically study the role of the several available approximation to deal with Coulomb correlations. In papers [1] and [2] the Hartree-Fock approximation was used, and in [3] Hubbard's approach for narrow d- band was applied in the context of the spin polarization. This calculation [3] was performed in the limit of large I/Δ (Coulomb interation to band width) and in a sense is a generalization of Hubbard and Jain's calculation [5] of the magnetic susceptibility of a strongly correlated narrow band.

The important feature of this calculation [3] is that effective exchange couplings (different in nature from those obtained within the Hartree-Fock approximation) where obtained, reflecting clearly the correlation effects introduced by higher order treatement of the equations of motion. It must be remembered [3] that the k,k' dependence of the exchange coupling (or in Wannier representation the "Kinetic energy" like character coupling) was the source of this effective exchange. In this paper we discuss Roth's [6] variational method as applied to the spin polarization problem. This calculation extends Schweitzer [7] approach for the magnetic susceptibility of a d-electron problem to hybridized bands and more complex "external" perturbations. Since the main result of Roth's approach [6] is to introduce in Hubbard's method [8] band shift effects (k-independent shifts and one-electron energy renormalizations) we expected to be able of discussing the effect of impurity sacattering in these parameters.

It is also pointed out some difficulties of Roth's procedure [6] in discussing certain correlation functions involved in the calculation of the effect of impurity scattering in the one- electron energy renormalization. A detailed discussion of these difficulties will be presented elsewhere [9] . The plan of this paper is a follows: in paragraph I the problem is formulated and the involved propagators are calculated.Paragraph II is the solution of the self-consistency problem, within some simplifying approximations, and the final result for the spin polarization is obtained in terms of pure host quantities and the exchange parameters. In the appendices a comparison to Hubbard's approach is presented together with some details of the calculation.

I. FORMULATION OF THE PROBLEM

a) Hamiltonian and general results of Roth's method

The transition metal-like host is described by the following hamiltonian:

$$\mathcal{H}_0 = \sum_{i,j,\sigma} T^{(s)}_{ij}\, c^+_{i\sigma} c_{j\sigma} + \sum_{i,j,\sigma} T^{(d)}_{ij} d^+_{i\sigma}\, d_{j\sigma} + \sum_i n^{(d)}_{i\uparrow}\, n^{(d)}_{i\downarrow} + \sum_{i,\sigma} \{V_{sd}\, c^+_{i\sigma} d_{i\sigma} + V_{ds}\, d^+_{i\sigma}\, c_{i\sigma}\} \qquad (1)$$

where s-d mixing is taken as a constant for simplicity.

The localized spin is supposed to be coupled to the conduction band through:

$$\mathcal{H}_{imp} = \sum_{i,j,\sigma} J^{(s)}(R_i,R_j) \langle S^z\rangle\sigma\; c^+_{i\sigma}\, c_{j\sigma} + \sum_{i,j,\sigma} J^{(d)}(R_i,R_j)\langle S^z\rangle\sigma\; d^+_{i\sigma} d_{j\sigma} \qquad (2)$$

where a k, k' dependent exchange coupling is considered. The total hamiltonian is then $H = H_o + H_{imp}$. It is purpose of this paragraph to calculate the one-electron propagator $G^{dd}_{ij}(\omega) = \langle\langle d_{i\sigma}; d^{+}_{j\sigma}\rangle\rangle_{\omega}$ to first order in the exchange coupling. Since electron-electron correlations are present one needs some kind of approximate treatment. In this paper we chose Roth's variational method [6] suitably applied to separate first order effects [7] . For a given basis set of propagators, Roth's equation for the corresponding propagators are (in matrix form):

$$\omega\, \hat{G}(\omega) = \frac{1}{2\pi}\hat{N} + \hat{K}\,.\,\hat{G}(\omega) \qquad (3\text{-a})$$

where the $\hat{K}$ matrix is defined through:

$$\hat{E} = \hat{K}\,.\,\hat{N} \qquad (3\text{-b})$$

$$E_{ij} = \langle[[A_i,\mathcal{H}]_{(-)}, A^{+}_{j}]_{(+)}\rangle \quad \text{and} \quad N_{ij} = \langle[A_i, A^{+}_{j}]_{(+)}\rangle \qquad (3\text{-c})$$

Let us consider as zero order, the hamiltonian described by H_o. The solution of this problem has been discussed previously [10], [11], and we assume here that the involved matrices, propagators and correlations functions are known. Then the zero order equations are:

$$\omega\, \hat{G}^{(o)}(\omega) = \frac{1}{2\pi}\hat{N}^{(o)} + \hat{K}^{(o)}\circ\hat{G}^{(o)}(\omega) \qquad (4\text{-a})$$

with

$$\hat{K}^{(o)} = \hat{E}^{(o)}\circ(\hat{N}^{(o)})^{-1} \qquad (4\text{-b})$$

And the first order equations are:

$$\omega\, \hat{G}^{(1)}(\omega) = \frac{1}{2\pi}\hat{N}^{(1)} + \hat{K}^{(1)}.\hat{G}^{(o)}(\omega) + \hat{K}^{(o)}.\hat{G}^{(1)}(\omega) \qquad (5)$$

Using equations (4) one gets:

$$\{\omega\hat{I} - \hat{E}^{(o)}.(\hat{N}^{(o)})^{-1}\}.\ \hat{G}^{(1)}(\omega) = \frac{1}{2\pi}\hat{N}^{(1)} + \hat{K}^{(1)}.\hat{G}^{(o)}(\omega) \qquad (6)$$

Now it remains to calculate the matrix $\hat{K}^{(1)}$; from the general definition (3-b) one has:

$$\hat{E}^{(1)} = \hat{K}^{(o)}.\hat{N}^{(1)} + \hat{K}^{(1)}.\hat{N}^{(o)} \qquad (7\text{-a})$$

or alternatively:

$$\hat{K}^{(1)} = \hat{E}^{(1)}.(\hat{N}^{(o)})^{-1} - \hat{E}^{(o)}.(\hat{N}^{(o)})^{-1}.\hat{N}^{(1)}.(\hat{N}^{(o)})^{-1} \qquad (7\text{-b})$$

Since the propagator $\hat{G}^{(o)}(\omega)$ of the host metal is supposed to be known, and the matrices $\hat{E}^{(1)}$ and $\hat{N}^{(1)}$ can be calculated using the definitions (3-c), equations (6) and (7-b) completely specify the first order correction $\hat{G}^{(1)}(\omega)$ for a given basis set of operators.

b) *Application of the general method to transition hosts*

The natural basis set for the problem defined by the hamiltonian (1) is [10]:

$$\{\ c_{i\sigma};\ d_{i\sigma};\ n^{(d)}_{i-\sigma}\ d_{i\sigma}\ \} \qquad (8)$$

If we define:

$$\langle n_{i-\sigma}^{(d)} \rangle = \langle n_{-\sigma}^{(d)} \rangle + \Delta n_{i-\sigma}^{(d)}$$

where $\langle n_{-\sigma}^{(d)} \rangle$ is the self-consistent occupation number for the hos metal and $\Delta n_{i-\sigma}^{(d)}$ is the first order correction. One gets from (3-c):

$$\hat{N}^{(o)} = \left[\begin{array}{c|cc} \delta_{ij} & 0 & 0 \\ \hline 0 & \delta_{ij} & \langle n_{-\sigma}^{(d)} \rangle \delta_{ij} \\ 0 & \langle n_{-\sigma}^{(d)} \rangle \delta_{ij} & \langle n_{-\sigma}^{(d)} \rangle \delta_{ij} \end{array}\right] \tag{9-a}$$

$$\hat{N}^{(1)} = \left[\begin{array}{c|cc} 0 & 0 & 0 \\ \hline 0 & 0 & \Delta n_{i-\sigma}^{(d)} \delta_{ij} \\ 0 & \Delta n_{i-\sigma}^{(d)} \delta_{ij} & \Delta n_{i-\sigma}^{(d)} \delta_{ij} \end{array}\right] \tag{9-b}$$

and using (9-a):

$$(N^{(o)})^{-1} = \left[\begin{array}{c|cc} \delta_{ij} & 0 & 0 \\ \hline 0 & \dfrac{\delta_{ij}}{1 - \langle n_{-\sigma}^{(d)} \rangle} & -\dfrac{\delta_{ij}}{1 - \langle n_{-\sigma}^{(d)} \rangle} \\ 0 & -\dfrac{\delta_{ij}}{1 - \langle n_{-\sigma}^{(d)} \rangle} & \dfrac{\delta_{ij}}{\langle n_{-\sigma}^{(d)} \rangle (1 - \langle n_{-\sigma}^{(d)} \rangle)} \end{array}\right] \tag{9-c}$$

Now we calculate the energy matrices in zero and first order. Firstly define:

$$<S_{i-\sigma}^{(d)}> = \sum_{\ell} T_{i\ell}^{(d)} \{<d_{i-\sigma}^{+} d_{\ell-\sigma}> - <d_{\ell-\sigma}^{+} d_{i-\sigma}>\}$$

$$<V_{i-\sigma}> = V_{ds} <d_{i-\sigma}^{+} c_{i-\sigma}> - V_{sd} <c_{i-\sigma}^{+} d_{i-\sigma}> \qquad (10)$$

$$<J_{i-\sigma}^{(d)}> = \sum_{\ell} J^{(d)}(R_i,R_\ell) <S^z>_\sigma \{<d_{i-\sigma}^{+} d_{\ell-\sigma}> - <d_{\ell-\sigma}^{+} d_{i-\sigma}>\}$$

It should be noted that in zero-order, the quantities $<S_{i-\sigma}^{(d)}>$ and $<V_{i-\sigma}>$ vanish and this connected to translation invariance [5]. Also, $<J_{i-\sigma}^{(d)}>$ exist only in second order (the bracket is only non-vanishing in first order). Now using definition (3-c) one gets (cf. [10]):

$$\hat{E}^{(o)} = \left[\begin{array}{c|cc} T_{ij}^{(s)} & V_{sd}\,\delta_{ij} & <n_{-\sigma}^{(d)}> V_{sd}\,\delta_{ij} \\ \hline V_{ds}\,\delta_{ij} & T_{ij}^{(d)} + I<n_{-\sigma}^{(d)}>\delta_{ij} & \{T_{ij}^{(d)} + I\delta_{ij}\} <n_{-\sigma}^{(d)}> \\ <n_{-\sigma}^{(d)}>V_{ds}\,\delta_{ij} & \{T_{ij}^{(d)} + I\delta_{ij}\}<n_{-\sigma}^{(d)}> & I <n_{-\sigma}^{(d)}>\delta_{ij} + \tilde{\Lambda}_{ij}^{(o)\sigma} \end{array}\right] \qquad (11\text{-a})$$

where we have defined in general (to any order in the pertubation):

$$\tilde{\Lambda}_{ij}^{\sigma} = \Lambda_{ij}^{\sigma} + \{V_{ds} <d_{i-\sigma}^{+} c_{i-\sigma} n_{i\sigma}^{(d)}> + V_{sd} <c_{i-\sigma}^{+} d_{i-\sigma} n_{i\sigma}^{(d)}> - V_{sd} <c_{i-\sigma}^{+} d_{i-\sigma}>\}\delta_{ij}$$

(11-b)

and

$$\Lambda_{ij}^{\sigma} = T_{ij}^{(d)} \langle n_{i-\sigma}^{(d)} n_{j-\sigma}^{(d)} \rangle - T_{ij}^{(d)} \langle \left[d_{i-\sigma}^{+} d_{j-\sigma} + d_{j-\sigma}^{+} d_{i-\sigma} \right] d_{j\sigma}^{+} d_{i\sigma} \rangle$$

$$- \delta_{ij} \sum_{\ell} T_{i\ell}^{(d)} \{ \langle d_{\ell-\sigma}^{+} d_{i-\sigma} \rangle - \langle n_{i\sigma}^{(d)} d_{\ell-\sigma}^{+} d_{i-\sigma} \rangle - \langle n_{i\sigma}^{(d)} d_{i-\sigma}^{+} d_{\ell-\sigma} \rangle \} \qquad (11\text{-c})$$

One recognizes in (11-b) and (11-c) the formal expression of Roth's band shift, as corrected for s-d mixings effects [10] and in equation (11-a) it only appears the host metal band shifts (zero order). Now the first order energy matrix is easily calculated using the same procedure:

$$\left[\begin{array}{c|c|c} J^{(s)}(R_i,R_j)\langle S^z\rangle\sigma & 0 & \Delta n_{i-\sigma}^{(d)} V_{sd}\, \delta_{ij} \\ \hline 0 & I\Delta n_{i-\sigma}^{(d)} + J^{(d)}(R_i,R_j)\langle S^z\rangle\sigma & \Delta n_{j-\sigma}^{(d)} T_{ij}^{(d)} + I\Delta n_{i-\sigma}^{(d)}\, \delta_{ij} + \langle n_{-\sigma}^{(d)}\rangle J^{(d)}(R_i,R_j)\langle S^z\rangle\sigma \\ \hline \Delta n_{i-\sigma}^{(d)} V_{ds}\, \delta_{ij} & \begin{array}{l} \Delta n_{i-\sigma}^{(d)} T_{ij}^{(d)} + I\Delta n_{i-\sigma}^{(d)}\delta_{ij} \\ +\{ \langle S_{i-\sigma}^{(d)}\rangle^{(1)} + \langle V_{i-\sigma}\rangle^{(1)} \}\delta_{ij} \\ + \langle n_{-\sigma}^{(d)}\rangle J^{(d)}(R_i,R_j)\langle S^z\rangle\sigma \end{array} & \begin{array}{l} I\Delta n_{i-\sigma}^{(d)}\delta_{ij} + \langle n_{-\sigma}^{(d)}\rangle J^{(d)}(R_i,R_j)\langle S^z\rangle\sigma \\ + K_{ij}^{\sigma}(J^{(d)}) + \tilde{\Lambda}_{ij}^{(1)\sigma} \end{array} \end{array} \right] \qquad (12\text{-a})$$

where we have defined:

$$K^{\sigma}_{ij}(J^{(d)}) = J^{(d)}(R_i,R_j)\langle S^z\rangle\sigma \ \{\langle n^{(d)}_{i-\sigma}\ n^{(d)}_{j-\sigma}\rangle^{(o)} - \langle\left[d^{+}_{i-\sigma}d_{j-\sigma} + d^{+}_{j-\sigma}d_{i-\sigma}\right]d^{+}_{j\sigma}d_{i\sigma}\rangle^{(o)}\}$$

$$- \delta_{ij}\sum_{\ell} J^{(d)}(R_i,R_j)\langle S^z\rangle\sigma \ \{\langle d^{+}_{\ell-\sigma}\ d_{i-\sigma}\rangle^{(o)} - \langle n^{(d)}_{i\sigma}\ d^{+}_{\ell-\sigma}\ d_{i-\sigma}\rangle^{(o)} -$$

$$- \langle n^{(d)}_{i\sigma}\ d^{+}_{i-\sigma}\ d_{\ell-\sigma}\rangle^{(o)}\} \qquad (12\text{-b})$$

One should note that in (12-a) the first order band shift as generally defined by (11-b) and (11-c) is present together with terms involving the exchange interactions and zero order correlation functions (as defined in $K^{\sigma}_{ij}(J^{(d)})$). Since the zero-order problem is supposed to be solved, the function K^{σ}_{ij} is completely determined.

Introduce now the general definition (valid to any order in the perturbation):

$$\tilde{\Lambda}^{\sigma}_{ij} = \langle n^{(d)}_{i-\sigma}\rangle(1-\langle n^{(d)}_{j-\sigma}\rangle)\tilde{W}_{ij} + T^{(d)}_{ij}\ \langle n^{(d)}_{i-\sigma}\rangle\ \langle n^{(d)}_{j-\sigma}\rangle + \langle n^{(d)}_{i-\sigma}\rangle\langle\alpha_{i-\sigma}\rangle\delta_{ij}$$

where: $$\langle\alpha_{i-\sigma}\rangle = \langle S^{(d)}_{i-\sigma}\rangle + \langle V_{i-\sigma}\rangle \qquad (13\text{-b})$$

In first order will be used

$$\langle\alpha_{i-\sigma}\rangle^{(1)} = \alpha_{i-\sigma}$$

Now using the result (11-a) and (9-c) one gets:

$$\hat{K}^{(o)} = \hat{E}^{(o)}.(\hat{N}^{(o)})^{-1} = \left[\begin{array}{c|cc} T^{(s)}_{ij} & V_{sd}\,\delta_{ij} & 0 \\ \hline V_{ds}\,\delta_{ij} & T^{(d)}_{ij} & I\delta_{ij} \\ \cline{2-3} \langle n^{(d)}_{-\sigma}\rangle V_{ds}\,\delta_{ij} & \langle n^{(d)}_{-\sigma}\rangle (T^{(d)}_{ij}-\tilde{W}^{(o)\sigma}_{ij}) & I\delta_{ij}+\tilde{W}^{(o)\sigma}_{ij} \end{array}\right] \quad (14\text{-a})$$

the matrix $\hat{K}^{(o)}$ (14-a) is nothing more that result for the pure host [10]. Consequently one gets for the left-hand side of (6):

$$\omega\hat{I} - \hat{K}^{(o)} = \left[\begin{array}{c|cc} \omega\delta_{ij} - T^{(s)}_{ij} & -V_{sd}\,\delta_{ij} & 0 \\ \hline -V_{ds}\,\delta_{ij} & \omega\delta_{ij} - T^{(d)}_{ij} & -I\,\delta_{ij} \\ \cline{2-3} -\langle n^{(d)}_{-\sigma}\rangle V_{ds}\,\delta_{ij} & -\langle n^{(d)}_{-\sigma}\rangle (T^{(d)}_{ij}-\tilde{W}^{(o)\sigma}_{ij}) & (\omega-I)\delta_{ij}-\tilde{W}^{(o)\sigma}_{ij} \end{array}\right] \quad (14\text{-b})$$

The matrix $\hat{G}(\omega)$ associated to the basis set (8) can be written as:

$$\hat{G}(\omega) = \begin{bmatrix} G^{ss}_{ij}(\omega) & G^{s1}_{ij}(\omega) & G^{s2}_{ij}(\omega) \\ G^{1s}_{ij}(\omega) & G^{11}_{ij}(\omega) & G^{12}_{ij}(\omega) \\ G^{2s}_{ij}(\omega) & G^{21}_{ij}(\omega) & G^{22}_{ij}(\omega) \end{bmatrix} \quad (15)$$

where we denoted by 1 the operator $d_{i\sigma}$ and by 2 the operator $n^{(d)}_{i-\sigma}\,d_{i\sigma}$. Now we explicitly evaluate the matrices $\hat{E}^{(1)}.(\hat{N}^{(0)})^{-1}$ and $\hat{E}^{(0)}.(\hat{N}^{(0)})^{-1}$. $N^{(1)}.(N^{(0)})^{-1}$ which are necessary to calculate the matrix $\hat{K}^{(1)}$. One

Obtains:

$$
\tilde{E}^{(1)}.(\tilde{N})^{-1} = \left[\begin{array}{c|c|c}
J^{(s)}(R_i,R_j)\langle S^z\rangle_\sigma & -\dfrac{\Delta n^{(d)}_{i-\sigma}V_{sd}\,\delta_{ij}}{1-\langle n^{(d)}_{-\sigma}\rangle} & \dfrac{\Delta n^{(d)}_{i-\sigma}\,V_{sd}\,\delta_{ij}}{\langle n^{(d)}_{-\sigma}\rangle\,(1-\langle n^{(d)}_{-\sigma}\rangle)} \\
\hline
0 & J^{(d)}(R_i,R_j)\langle S^z\rangle_\sigma - \dfrac{\Delta n^{(d)}_{j-\sigma}T^{(d)}_{ij}}{1-\langle n^{(d)}_{-\sigma}\rangle} & I\,\Delta n^{(d)}_{i-\sigma}\dfrac{\delta_{ij}}{\langle n^{(d)}_{-\sigma}\rangle} + \dfrac{\Delta n^{(d)}_{j-\sigma}\,T^{(d)}_{ij}}{\langle n^{(d)}_{-\sigma}\rangle\,(1-\langle n^{(d)}_{-\sigma}\rangle)} \\
\hline
\Delta n^{(d)}_{i-\sigma}V_{ds}\,\delta_{ij} & \begin{array}{l} \dfrac{\langle n^{(d)}_{-\sigma}\rangle J^{(d)}(R_i,R_j)-\langle n^{(d)}_{-\sigma}\rangle J^{(d)}(R_i,R_j)\delta_{ij}}{1-\langle n^{(d)}_{-\sigma}\rangle}\langle S^z\rangle_\sigma \\ + \dfrac{\alpha_{i-\sigma}\delta_{ij}}{1-\langle n^{(d)}_{-\sigma}\rangle} - \dfrac{K^{\sigma}_{ij}(J^{(d)})+\tilde{\Lambda}^{\sigma}_{ij}\,^{(1)}}{1-\langle n^{(d)}_{-\sigma}\rangle} + \\ + \dfrac{\Delta n^{(d)}_{i-\sigma}\,T^{(d)}_{ij}}{1-\langle n^{(d)}_{-\sigma}\rangle} \end{array} & \begin{array}{l} \dfrac{J^{(d)}(R_i,R_j)\delta_{ij}-\langle n^{(d)}_{-\sigma}\rangle J^{(d)}(R_i,R_j)}{1-\langle n^{(d)}_{-\sigma}\rangle}\langle S^z\rangle_\sigma \\ - \dfrac{\alpha_{i-\sigma}\,\delta_{ij}}{1-\langle n^{(d)}_{-\sigma}\rangle} + \dfrac{K^{\sigma}_{ij}\,(J^{(d)}) + \tilde{\Lambda}^{\sigma}_{ij}}{\langle n^{(d)}_{-\sigma}\rangle(1-\langle n^{(d)}_{-\sigma}\rangle)} \\ + I\,\dfrac{\Delta n^{(d)}_{i-\sigma}}{\langle n^{(d)}_{-\sigma}\rangle}\,\delta_{ij} - T^{(d)}_{ij}\,\dfrac{\Delta n^{(d)}_{i-\sigma}}{1-\langle n^{(d)}_{-\sigma}\rangle} \end{array}
\end{array}\right] \qquad (16\text{-}a)
$$

and

$$\hat{E}^{(o)} \cdot (\hat{N}^{(o)})^{-1} \cdot \hat{N}^{(1)} \cdot (\hat{N}^{(o)})^{-1} = \left[\begin{array}{c|c|c} 0 & -\dfrac{V_{sd}\,\Delta n^{(d)}_{i-\sigma}\,\delta_{ij}}{1-\langle n^{(d)}_{-\sigma}\rangle} & \dfrac{V_{sd}\,\Delta n^{(d)}_{i-\sigma}\,\delta_{ij}}{\langle n^{(d)}_{-\sigma}\rangle(1-\langle n^{(d)}_{-\sigma}\rangle)} \\ \hline 0 & -\dfrac{\Delta n^{(d)}_{j-\sigma}\,T^{(d)}_{ij}}{1-\langle n^{(d)}_{-\sigma}\rangle} & I\,\dfrac{\Delta n^{(d)}_{i-\sigma}}{\langle n^{(d)}_{-\sigma}\rangle}\,\delta_{ij} + \dfrac{\Delta n^{(d)}_{j-\sigma}\,T^{(d)}_{ij}}{\langle n^{(d)}_{-\sigma}\rangle(1-\langle n^{(d)}_{-\sigma}\rangle)} \\ \hline 0 & -\dfrac{\langle n^{(d)}_{-\sigma}\rangle(T^{(d)}_{ij}-\tilde{W}^{(o)}_{ij})}{1-\langle n^{(d)}_{-\sigma}\rangle}\,\Delta n^{(d)}_{j-\sigma} & I\,\dfrac{\Delta n^{(d)}_{i-\sigma}}{\langle n^{(d)}_{-\sigma}\rangle}\,\delta_{ij} + \dfrac{\tilde{W}^{(o)}_{ij} + \langle n^{(d)}_{-\sigma}\rangle\,T^{(d)}_{ij}}{\langle n^{(d)}_{-\sigma}\rangle\,(1-\langle n^{(d)}_{-\sigma}\rangle)}\,\Delta n^{(d)}_{j-\sigma} - 2\,\dfrac{\tilde{W}^{(o)}_{ij}}{1-\langle n^{(d)}_{-\sigma}\rangle}\,\Delta n^{(d)}_{j-\sigma} \end{array}\right] \tag{16-b}$$

Now using (7-b) we obtain for the $\tilde{K}^{(1)}$ matrix:

$$\tilde{K}^{(1)} = \left[\begin{array}{c|cc} J^{(s)}(R_i,R_j)\langle S^z\rangle\sigma & 0 & 0 \\ \hline 0 & J^{(d)}(R_i,R_j)\langle S^z\rangle\sigma & 0 \\ \cline{2-3} n^{(d)}_{i-\sigma} V_{ds}\ \delta_{ij} & A^{\sigma}_{ij} & B^{\sigma}_{ij} \end{array}\right] \qquad (17\text{-a})$$

where we have defined A^{σ}_{ij} as:

$$A^{\sigma}_{ij} = \frac{\{\langle n^{(d)}_{-\sigma}\rangle J^{(d)}(R_i,R_j) - \langle n^{(d)}_{-\sigma}\rangle J^{(d)}(R_i,R_i)\delta_{ij}\}\ \langle S^z\rangle\sigma - K^{\sigma}_{ij}(J^{(d)})}{1 - \langle n^{(d)}_{-\sigma}\rangle} +$$

$$+ \frac{\alpha_{i-\sigma}\delta_{ij}}{1-\langle n^{(d)}_{-\sigma}\rangle} + T^{(d)}_{ij}\ \frac{\Delta n^{(d)}_{i-\sigma} + \langle n^{(d)}_{-\sigma}\rangle \Delta n^{(d)}_{j-\sigma}}{1 - \langle n^{(d)}_{-\sigma}\rangle} - \frac{\langle n^{(d)}_{-\sigma}\rangle \tilde{W}^{(o)}_{ij}}{1-\langle n^{(d)}_{-\sigma}\rangle}\Delta n^{(d)}_{j-\sigma} - \frac{\tilde{\Lambda}^{(1)\sigma}_{ij}}{1 - \langle n^{(d)}_{-\sigma}\rangle} \qquad (17\text{-b})$$

The explicit form of B^{σ}_{ij} will not be presented since this term does not contribue in the infinite repulsion limit (cf. below). Now we rewrite equation (17-b) in more convinient way:

$$A^{\sigma}_{ij} = \Delta n^{(d)}_{i-\sigma}\ \frac{(1 - \langle n^{(d)}_{-\sigma}\rangle) T^{(d)}_{ij} + \langle n^{(d)}_{-\sigma}\rangle \tilde{W}^{(o)}_{ij}}{1 - \langle n^{(d)}_{-\sigma}\rangle} +$$

$$+ \frac{\langle n^{(d)}_{-\sigma}\rangle \{J^{(d)}(R_i,R_j) - J^{(d)}(R_i,R_i)\delta_{ij}\}\ \langle S^z\rangle\sigma - K^{\sigma}_{ij}(J^{(d)})}{1 - \langle n^{(d)}_{-\sigma}\rangle} - \frac{M^{\sigma}_{ij}}{1 - \langle n^{(d)}_{-\sigma}\rangle} \qquad (18\text{-a})$$

where we have defined:

$$M^{\sigma}_{ij} = \tilde{\Lambda}^{(1)\sigma}_{ij} - <n^{(d)}_{-\sigma}> \{\Delta n^{(d)}_{i-\sigma} + \Delta n^{(d)}_{j-\sigma}\} T^{(d)}_{ij} + <n^{(d)}_{-\sigma}> \{\Delta n^{(d)}_{i-\sigma} + \Delta n^{(d)}_{j-\sigma}\} \tilde{W}^{(o)}_{ij} - $$

$$- \alpha_{i-\sigma}\, \delta_{ij} \qquad (18\text{-b})$$

c) *Determination and solution of the equations of motion (strong correlation limit)*

Using equations (6), (14-b), (17-a) and (18-a) one obtains the following equations of motion for the first order propagators:

$$\omega\, G^{11(1)}_{ij}(\omega) = \sum_{\ell} T^{(d)}_{i\ell}\, G^{11(1)}_{\ell j}(\omega) + I\, G^{21(1)}_{ij}(\omega) + V_{ds}\, G^{S1(1)}_{ij}(\omega) +$$

$$+ \sum_{\ell} J^{(d)}(R_i, R_{\ell}) <S^z> \sigma\, G^{11(o)}_{\ell j}(\omega) \qquad (19\text{-a})$$

$$\omega\, G^{S1(1)}_{ij}(\omega) = \sum_{\ell} T^{(s)}_{i\ell}\, G^{S1(1)}_{\ell j}(\omega) + V_{ds}\, G^{11(1)}_{ij}(\ ) + \sum_{\ell} J^{(s)}(R_i, R_{\ell}) <S^z> \sigma\, G^{S1(o)}_{\ell j}(\omega)$$

$$(19\text{-b})$$

$$(\omega - I) G^{21(1)}_{ij}(\omega) = <n^{(d)}_{-\sigma}> \sum_{\ell} (T^{(d)}_{i\ell} - \tilde{W}^{(o)\sigma}_{i\ell}) G^{11(1)}_{\ell j}(\omega) + \sum_{\ell} \tilde{W}^{(o)\sigma}_{i\ell} G^{21(1)}_{\ell j}(\omega) +$$

$$+ <n^{(d)}_{-\sigma}> V_{ds}\, G^{S1(1)}_{ij}(\omega) + \frac{1}{2\pi}\, \Delta n^{(d)}_{i-\sigma} \left\{ \delta_{ij} + \sum_{\ell} \frac{(1 - <n^{(d)}_{-\sigma}>) T^{(d)}_{i\ell} + <n^{(d)}_{-\sigma}> \tilde{W}^{(o)\sigma}_{i\ell}}{1 - <n^{(d)}_{-\sigma}>} G^{11(o)}_{\ell j}(\omega) + \right.$$

cont.

$$V_{ds}\, G^{s1(o)}_{ij}(\omega) \Bigg\} + \sum_{\ell} \frac{\langle n^{(d)}_{-\sigma}\rangle \{J^{(d)}(R_i,R_\ell) - J^{(d)}(R_i,R_i)\delta_{i\ell}\}\langle S^z\rangle\sigma - K_{i\ell}(J^{(d)})}{1 - \langle n^{(d)}_{-\sigma}\rangle} G^{11(o)}_{\ell j}(\omega)$$

$$- \sum_{\ell} \frac{M^{\sigma}_{i\ell}}{1 - \langle n^{(d)}_{-\sigma}\rangle} G^{11(o)}_{\ell j}(\omega) + \sum_{\ell} B_{i\ell}\, G^{21(o)}_{\ell j}(\omega) \qquad (19\text{-c})$$

Now it should be noted that equations (19-a) and (19-b) are <u>exact equations</u> of motion(as in[3]), the approximations characterizing the varational method being incorporated in (19-c). Next step is the solution of the coupled equations (19)in the limit of strong correlations. We start Fourier transforming equations (19-a) and (19-b); one gets:

$$(\omega-\varepsilon^{(d)}_k)G^{11(1)}_{kk'}(\omega) = IG^{21(1)}_{kk'}(\omega) + V_{ds}\, G^{s1(1)}_{kk'}(\omega) + \\ + \sum_{k''} J^{(d)}(k,k'')\langle S^z\rangle\sigma\, G^{11(o)}_{k''k'}(\omega) \qquad (20)$$

$$(\omega-\varepsilon^{(s)}_k)G^{s1(1)}_{kk'}(\omega) = V_{sd}\, G^{11(1)}_{kk'}(\omega) + \sum_{k''} J^{(s)}(k,k'')\langle S^z\rangle\sigma\, G^{s1(o)}_{k''k'}(\omega)$$

The involved zero-order propagators are known and diagonal in Bloch representation; they are given by [10] :

$$G^{11(o)}_{kk'}(\omega) = \frac{1}{2\pi}\,\delta_{kk'}\,\bar{n}^{(d)}\, g_k(\omega) = \frac{1}{2\pi}\,\delta_{kk'}\,\frac{\bar{n}^{(d)}}{\omega-\bar{n}^{(d)}\tilde{\varepsilon}^{(d)}_k - \langle n^{(d)}\rangle\,\tilde{W}^{(o)}_k} \qquad (21\text{-a})$$

$$G^{s1(o)}_{kk'}(\omega) = \frac{1}{2\pi}\,\delta_{kk'}\,\frac{\bar{n}^{(d)}\;V_{sd}}{\omega - \varepsilon^{(s)}_k}\,g_k(\omega) \tag{21-b}$$

where we have defined:

$$\bar{n}^{(d)} = 1 - \langle n^{(d)}\rangle$$

$$\tilde{\varepsilon}^{(d)}_k = \varepsilon^{(d)}_k + \frac{|V_{sd}|^2}{\omega-\varepsilon^{(s)}_k}$$

$\tilde{W}^{(0)}_k$ being the pure host "band shift", assuming a paramagnetic host.

Using these results one obtains instead of (20):

$$(\omega - \varepsilon^{(d)}_k)G^{11(1)}_{kk'}(\omega) = IG^{21(1)}_{kk'}(\omega) + V_{ds}\,G^{s1(1)}_{kk'}(\omega) + \frac{1}{2\pi}\,J^{(d)}(k,k')\langle S^z\rangle\sigma\,\bar{n}^{(d)}\,g_{k'}(\omega) \tag{22-a}$$

$$(\omega-\varepsilon^{(s)}_k)G^{s1(1)}_{kk'}(\omega) = V_{sd}\,G^{11(1)}_{kk'}(\omega) + \frac{1}{2\pi}\,J^{(s)}(k,k')\langle S^z\rangle\sigma\,\bar{n}^{(d)}\,\frac{1}{\omega-\varepsilon^{(s)}_{k'}}\,V_{sd}g_{k'}(\omega) \tag{22-b}$$

Using the equation of motion for $G^{21(1)}_{kk'}(\omega)$ one gets:

$$(\omega-I-\tilde{W}^{(o)}_k)G^{21(1)}_{kk'}(\omega) = \langle n^{(d)}\rangle(\varepsilon^{(d)}_k-\tilde{W}^{(o)}_k)G^{11(1)}_{kk'}(\omega) + \langle n^{(d)}\rangle V_{ds}\,G^{s1(1)}_{kk'}(\omega) + + \frac{1}{2\pi}\,\Delta n^{-\sigma(d)}_{kk'}{}_{\omega}\,g_{k'}(\omega) + \frac{1}{2\pi}\Big[\langle n^{(d)}\rangle\{J^{(d)}(k,k') - \sum_{k''}J^{(d)}(k'',k''+k-k')\}\langle S^z\rangle\sigma - - K^{\sigma}_{kk'}(J^{(d)})\Big]\,g_{k'}(\omega) - \frac{1}{2\pi}\,M_{kk'}\,g_{k'}(\omega) + B_{kk'}g^{21(o)}_{k'}(\omega) \tag{22-c}$$

where the term $\Delta n_{kk'}^{-\sigma(\omega)}\omega\, g_{k'}(\omega)$ was obtained using equations (21-a) and (21-b) in order to transform the term proportional to $\Delta n_{i-\sigma}^{(d)}$ in equation (19-c).

Now we take the limit of $I \to \infty$ (strongly correlated limit). One knows form previous calculations that $\lim_{I \to \infty} g_{k'}^{21(o)} = 0$, so one gets from (22-c):

$$\lim_{I \to \infty} IG_{kk'}^{21(1)}(\omega) = - \langle n^{(d)}\rangle(\varepsilon_k - \tilde{W}_k^{(o)})\, G_{kk'}^{11(1)}(\omega) - \langle n^{(d)}\rangle V_{ds}\, G_{kk'}^{s1(1)}(\omega) -$$

$$- \frac{1}{2\pi}\Delta n_{kk'}^{-\sigma(d)}\omega\, g_{k'}(\omega) - \frac{1}{2\pi}\Big[\langle n^{(d)}\rangle \{J^{(d)}(k,k') - \sum_{k''} J^{(d)}(k'',k'' + k-k')\}$$

$$\langle S^z\rangle\sigma - K_{kk'}^{\sigma}(J^{(d)})\Big]\, g_{k'}(\omega) + \frac{1}{2\pi} M_{kk'}^{\sigma}\, g_{k'}(\omega) \qquad (23)$$

Next step is to substitute $IG_{kk'}^{21}(\omega)$ as given by (23) into equation (22-a) and solve the coupled equation formed by (22-b) and this new equation (22-a); one gets:

$$G_{kk'}^{11(1)}(\omega) = \frac{1}{2\pi} g_k(\omega)\, J_{eff}^{(R)}(k,k')\langle S^z\rangle\sigma\, g_{k'}(\omega) -$$

$$- \frac{1}{2\pi} g_k(\omega)\omega\;\; \Delta n_{kk'}^{-\sigma(d)} g_{k'}(\omega) + \frac{1}{2\pi} g_k(\omega)\, M_{kk'}^{\sigma}\, g_{k'}(\omega) \;+$$

$$+ \frac{1}{2\pi} g_k(\omega)\, V_{ds} \frac{1}{\omega - \varepsilon_k^{(s)}} (\bar{n}^{(d)})^2\, J^{(s)}(k,k')\, \langle S^z\rangle\sigma \frac{1}{\omega - \varepsilon_{k'}^{(s)}} V_{sd}\, g_{k'}(\omega) \qquad (24\text{-a})$$

where we have defined Roth's method effective d-exchange:

$$J_{eff}^{(R)}(k,k') = \overline{n}^{(d)} J^{(d)}(k,k') + \langle n^{(d)}\rangle \left[\sum_{k''} J^{(d)}(k'',k''+k-k') - J^{(d)}(k,k')\right] + $$

$$+ \overline{K}_{kk'}(J^{(d)}) , \qquad (24\text{-}b)$$

where $\overline{K}_{kk'}(J^{(d)})$being defined without the factor $\langle S^z\rangle\sigma$.

One should note in (24-a) the formal similarity of these results to those obtained using Hubbard's method [3].A detailed comparison between these results will be made in Appendix A.

II. SELF-CONSISTENCY PROBLEM

a) Correlation functions involved in equations (24)

Equation (24) involves parameters $\Delta n_q^{-\sigma(d)}$ and $M_{kk'}^{\sigma}$ that should be self-consistently determined in terms of the exchange couplings $J^{(s)}$ and $J^{(d)}$ and the host metal band structure.

First of all we want to emphasize that in $J_{eff}^{(R)}(k,k')$ all the involved quantities are known from pure host metal result (cf. equations (24-b) and (12-b)). Now the explicit form of $M_{kk'}^{\sigma}$ reads:

$$M_{kk'}^{\sigma} = \tilde{\Lambda}_{kk'}^{(1)\sigma} - \langle n_{-\sigma}^{(d)}\rangle \{\varepsilon_k^{(d)} + \varepsilon_{k'}^{(d)} - \tilde{W}_k^{(o)} - \tilde{W}_{k'}^{(o)}\} \Delta n_{kk'}^{(d)} -$$

$$- \alpha_{kk'}^{-\sigma} \qquad (25\text{-}a)$$

where the first order "band shift" $\tilde{\Lambda}_{kk'}^{(1)\sigma}$ is given by:

$$\tilde{\Lambda}_{kk'}^{(1)\sigma} = \Delta_{kk'}^{(1)\sigma}(V) - \Delta_{kk'}^{(1)\sigma}(T) + R_{kk'}^{(1)}(T) \qquad (25\text{-}b)$$

these quantities being defined as:

$$\Delta^{(1)\sigma}_{kk'}(V) = \sum_i e^{i(k-k').R_i} \{V_{ds} <n^{(d)}_{i\sigma} d^+_{i-\sigma} c_{i-\sigma}>^{(1)} + $$

$$+ V_{sd} <n^{(d)}_{i\sigma} c^+_{i-\sigma} d_{i-\sigma}>^{(1)} - V_{sd} <c^+_{i-\sigma} d_{i-\sigma}>^{(1)} \} \quad (26\text{-a})$$

$$\Delta^{(1)\sigma}_{kk'}(T) = \sum_{i,\ell} e^{i(k-k').R_i} T^{(d)}_{i\ell} \{ <d^+_{\ell-\sigma} d_{i-\sigma}>^{(1)} - <n^{(d)}_{i\sigma} d^+_{\ell-\sigma} d_{i-\sigma}>^{(1)} -$$

$$- <n^{(d)}_{i\sigma} d^+_{i-\sigma} d_{\ell-\sigma}>^{(1)} \} \quad (26\text{-b})$$

$$R^{(1)}_{kk'}(T) = \sum_{i,j} e^{ik.R_i} e^{-ik'.R_j} T^{(d)}_{ij} \{ <n^{(d)}_{i-\sigma} n^{(d)}_{j-\sigma}>^{(1)} -$$

$$- <\left[d^{(d)}_{i-\sigma} d_{j-\sigma} + d^+_{j-\sigma} d_{i-\sigma} \right] d^+_{j\sigma} d_{i\sigma}>^{(1)} \} \quad (26\text{-c})$$

Using the identity:

$$<n^{(d)}_{i-\sigma} n^{(d)}_{j-\sigma}>^{(1)} = <\Delta n^{(d)}_{i-\sigma} \Delta n^{(d)}_{j-\sigma}>^{(1)} + <n^{(d)}> \{\Delta n^{(d)}_{i-\sigma} + \Delta n^{(d)}_{j-\sigma} \}$$

equation (26-c) can be rewritten as:

$$R^{(1)}_{kk'}(T) = <n^{(d)}_{-\sigma}> \{\varepsilon^{(d)}_k + \varepsilon^{(d)}_{k'}\} \Delta n^{-\sigma(d)}_{kk'} + \tilde{R}^{(1)}_{kk'}(T) \quad (27\text{-a})$$

$$\tilde{R}^{(1)}_{kk'}(T) = \sum_{i,j} e^{ik.R_i} e^{-ik'.R_j} T^{(d)}_{ij} \{ <\Delta n^{(d)}_{i-\sigma} \Delta n^{(d)}_{j-\sigma}>^{(1)} -$$

$$- < \left[d^{+}_{i-\sigma} d_{j-\sigma} + d^{+}_{j-\sigma} d_{i-\sigma} \right] d^{+}_{j\sigma} d_{i\sigma} >^{(1)} \qquad (27\text{-b})$$

A simpler version of (25-a) is then:

$$M^{\sigma}_{kk'} = <n^{(d)}> \{\tilde{W}^{(o)}_{k} + \tilde{W}^{(o)}_{k'}\} \Delta n^{-\sigma(d)}_{kk'} + \Delta^{(1)\sigma}_{k-k'}(V) - V^{-\sigma}_{k-k'} - \Delta^{(1)\sigma}_{k-k'}(T) -$$

$$- S^{\sigma}_{k-k'} + \tilde{R}_{kk'}(T) \qquad (28)$$

where we used:

$$\alpha^{-\sigma}_{kk'} = V^{-\sigma}_{k-k'} + S^{-\sigma}_{k-k'}$$

(cf. equation (13-b))

b) *Connection between the correlation functions and first order propagators*

From definitions (10) one has:

$$S^{-\sigma}_{k-k'} = S^{-\sigma}_{q} = \sum_{k} (\varepsilon^{(d)}_{k+q} - \varepsilon^{(d)}_{k}) F_{\omega} \left[G^{11(1)}_{k+q,k;-\sigma}(\omega) \right] \qquad (29\text{-a})$$

which completely defines $S^{-\sigma}_{q}$ in terms of the first order propagator $G^{11(1)}_{kk'}(\omega)$. Again from (10) one has:

$$V_{k-k'}^{-\sigma} = V_q^{-\sigma} = V_{ds} \sum_k F_\omega \left[G_{k+q,k;-\sigma}^{s1(1)}(\omega)\right] - V_{sd} \sum_k F_\omega \left[G_{k+q,k;-\sigma}^{1s(1)}(\omega)\right] \tag{29-b}$$

Expression (29-b) involves both the $G_{kk'}^{s1}$ and $G_{kk'}^{1s}$ propagators, which in principle can be obtained from the general equation (6) together whith (14-b) and (17-a). However in contrast to Hubbard's approach [3] here one just needs to know the $G_{kk'}^{s1}$ propagator. In order to see that we compute the quantity $\Delta_{k-k'}^{(1)\sigma}(V)$. One gets from (26-a):

$$- \Delta_{k-k'}^{(1)\sigma}(V) = - \Delta_q^{(1)\sigma}(V) = V_{sd} \sum_k F_\omega \left[G_{k+q,k;-\sigma}^{1s(1)}(\omega)\right] - V_{sd} \sum_k F_\omega \left[G_{k+q,k;-\sigma}^{2s(1)}(\omega)\right]$$

$$- V_{ds} \sum_k F_\omega \left[G_{k+q,k;-\sigma}^{s2(1)}(\omega)\right] \tag{29-c}$$

Using the equations of motion for the propagators $G_{kk'}^{2s(1)}$ and $G_{kk'}^{s2(1)}$, one can show that (cf. Appendix B) $\lim_{I \to \infty} G_{kk'}^{2s(1)} = \lim_{I \to \infty} G_{kk'}^{s2(1)} = 0$, thus reducing expression (29-c) to:

$$- \Delta_q^{(1)\sigma}(V) = V_{sd} \sum_k F_\omega \left[G_{k+q,k;-\sigma}^{1s(1)}(\omega)\right] \tag{29-d}$$

Introducing the quantity $\Omega_q^{-\sigma}(V)$ as

$$\Omega_q^{-\sigma}(V) = V_q^{-\sigma} - \Delta_q^{(1)\sigma}(V) \tag{30-a}$$

one has:

$$\Omega_q^{-\sigma}(V) = V_{ds} \sum_k F_\omega \left[G_{k+q,k;-\sigma}^{s1(1)}(\omega)\right] \tag{30-b}$$

Expression (30-b) shows that all the quantities involving the mixing are completely determined in terms of the propagator $G^{s1(1)}_{kk'}(\omega)$.

Now the correlation function $\Delta^{(1)\sigma}_{k-k'}$ (T) is given by:

$$\Delta^{(1)\sigma}_{k-k'}(T) = \Delta^{(1)\sigma}_{q}(T) = \sum_k \varepsilon^{(d)}_k \{ F_\omega \left[G^{11(1)}_{k+q,k;-\sigma}(\omega)\right] - F_\omega \left[G^{21(1)}_{k+q,k;-\sigma}(\omega)\right] \}$$

$$- \sum_k \varepsilon^{(d)}_{k+q} F_\omega \left[G^{12(1)}_{k+q,k;-\sigma}(\omega) \right] \qquad (31\text{-a})$$

Quite similarly (cf. (22-c) and Appendix B) one gets $\lim_{I \to \infty} G^{21(1)}_{kk'} = \lim_{I \to \infty} G^{12(1)}_{kk'} = 0$, reducing expression (31-a) to just the first term. Introducing now:

$$\Omega^{-\sigma}_q(T) = S^{-\sigma}_q + \Delta^{(1)\sigma}_q(T) \qquad (31\text{-b})$$

one has:

$$\Omega^{-\sigma}_q(T) = \sum_k \varepsilon^{(d)}_{k+q} \; F_\omega \left[G^{11(1)}_{k+q,k;-\sigma}(\omega) \right] \qquad (31\text{-c})$$

So using (31-b), (30-a) one obtains for (28):

$$M^{\sigma}_{k+q,k} = \langle n^{(d)} \rangle \{ \tilde{W}^{(o)}_{k+q} + \tilde{W}^{(o)}_k \} \, \Delta n^{-\sigma(d)}_q - \Omega^{-\sigma}_q(V) - \Omega^{-\sigma}_q(T) +$$

$$+ \tilde{R}^{(1)}_{k+q,k}(T) \qquad (31\text{-d})$$

where except for the last term, the quantities involved in (32) are completely determined by $G^{11(1)}_{kk'}$ and $G^{s1(1)}_{kk'}$. At this point we introduce the approximation of neglecting the $\tilde{R}^{(1)}_{k+q,k}(T)$ term of equation (31-d). In principle this term can be calculated following the prescription introduced by Roth; one defines operators B in such a way that from the propagators $\langle\langle A_i;B\rangle\rangle$ ($\{A_i\}$ the basis set) the involved correlation function functions can be obtained. This procedure however is mathematicaly very elaborate and introduces some types of ambiguities [9]. In this work we simply neglect this term, its calculation being left to a forthcoming work. In the pure host case this term corresponds to the k-dependent part of the band shift (which corresponds to a renormalization of the dispersion relation). In the impurity problem we expect that to neglect this term correspond to assume that the impurity scattering does not disturb the "effective tunnelling" [9] between atoms. So:

$$M^{\sigma}_{k+q,k} \cong \langle n^{(d)}\rangle\{\tilde{W}^{(o)}_{k+q} + \tilde{W}^{(o)}_{k}\}\Delta n^{-\sigma(d)}_{q} - \Omega^{-\sigma}_{q}(V) - \Omega^{-\sigma}_{q}(T) \qquad (32)$$

Then expression (32) includes only the effects due to scattering associated to the k-independent part of the band shift.

c) *Determination of* $\Omega^{-\sigma}_{q}(V)$ *and* $\Omega^{-\sigma}_{q}(T)$ *in terms of* $\Delta n^{-\sigma(d)}_{q}$

Using the simplified expression for $M^{\sigma}_{k+q,k}$ one gets for the $G^{11(1)}_{k+q,k}$ propagator.

$$G^{11(1)}_{k+q,k}(\omega) = \frac{1}{2\pi}\, g_{k+q}(\omega)\, J^{(R)}_{eff}(k,k')\, \langle S^{z}\rangle\sigma\, g_{k}(\omega) - \frac{1}{2\pi}\, g_{k+q}(\omega)\,\omega\, g_{k}(\omega)\, \Delta n^{-\sigma(d)}_{q}$$

cont.

$$+ \frac{1}{2\pi} g_{k+q}(\omega) <n^{(d)}>\{ \tilde{W}^{(o)}_{k+q} + \tilde{W}^{(o)}_{k}\} g_k(\omega) \Delta n_q^{-\sigma(d)} -$$

$$- \frac{1}{2\pi} g_{k+q}(\omega) g_k(\omega)\{ \Omega_q^{-\sigma}(V) + \Omega_q^{-\sigma}(T) \}+$$

$$+ \frac{1}{2\pi} |V_{sd}|^2 (\overline{n}^{(d)})^2 J^{(s)}(k+q,k) <S^z>\sigma \; g_{k+q}(\omega) \frac{1}{(\omega-\varepsilon^{(s)}_{k+q})(\omega-\varepsilon^{(s)}_{k})} g_k(\omega) \tag{33-a}$$

From equation (22-b) one gets the other propagator:

$$G^{s1(1)}_{k+q,k}(\omega) = \frac{V_{sd}}{\omega-\varepsilon^{(s)}_{k+q}} G^{11(1)}_{k+q,k}(\omega) + \frac{1}{2\pi} \frac{V_{sd}}{\omega-\varepsilon^{(s)}_{k+q}} J^{(s)}(k+q,k) <S^z>n^{(d)} \frac{1}{\omega-\varepsilon^{(s)}_{k}} g_k(\omega) \tag{33-b}$$

Now we follow the prescriptions defined in equations (30-b) and (31-c):

1º) Determination of Ω_q^{σ} (T)

Introducing the susceptibilities: (these definitions differ from the usual ones by a minus sign)

$$\chi_1(k,q) = \frac{1}{2\pi} F_\omega\{ g_{k+q}(\omega) g_k(\omega) \}$$

$$\tilde{\chi}_1(k,q) = \frac{1}{2\pi} F_\omega\{ \omega g_{k+q}(\omega) g_k(\omega) \} \tag{34}$$

and

$$\chi(k,q) = \frac{1}{2\pi} F_\omega\{ g_{k+q}(\omega) \frac{1}{(\omega-\varepsilon^{(s)}_{k+q})(\omega-\varepsilon^{(s)}_k)} g_k(\omega) \}$$

one gets from equations (33-a):

$$\Omega_q(T) = \langle S^z\rangle\sigma \sum_k J^{(R)}_{eff}(k+q,k)\ \varepsilon^{(d)}_{k+q}\ \chi_1(k,q) +$$

$$+ (\overline{n}^{(d)})^2|V_{sd}|^2\langle S^z\rangle\sigma\sum_k J^{(s)}(k+q,k)\ \varepsilon^{(d)}_{k+q}\ \chi(k,q) - \{ \sum_k \varepsilon^{(d)}_{k+q}\ \chi_1(k,q) -$$

$$- \sum_k \varepsilon^{(d)}_{k+q} \langle n^{(d)}\rangle \left[\tilde{W}^{(o)}_{k+q} + \tilde{W}^{(o)}_k \right] \chi_1(k,q) \}\Delta n^{-\sigma(d)}_q - \{\Omega_q^{-\sigma}(V) +$$

$$+ \Omega_q^{-\sigma}(T)\} \sum_k \varepsilon^{(d)}_{k+q}\ \chi_1(k,q) \qquad (35\text{-a})$$

Now we redefine things in order to simplify the self-consistency equations; let:

$$E^{(d)}_J(q) = \langle S^z\rangle\sigma \sum_k J^{(R)}_{eff}(k+q,k)\ \varepsilon^{(d)}_{k+q}\ \chi_1(k,q)$$

$$E^{(s)}_J(q) = (\overline{n}^{(d)})^2|V_{sd}|^2 \sum_k J^{(s)}(k+q,k)\ \varepsilon^{(d)}_{k+q}\ \chi(k,q)$$

$$E(q) = \sum_k \varepsilon^{(d)}_{k+q}\ \tilde{\chi}_1(k,q)$$

$$E_W(q) = \sum_k \varepsilon^{(d)}_{k+q} \langle n^{(d)}\rangle \{ \tilde{W}^{(o)}_{k+q} + \tilde{W}^{(o)}_k \} \chi_1(k,q) \qquad (35\text{-b})$$

and the "ocupation number":

$$N(q) = \sum_k \varepsilon^{(d)}_{k+q}\, \chi_1(k,q) \qquad (35\text{-c})$$

In terms of these quantities the first self-consistency relation reads:

$$\Omega^{\sigma}_{q}(T) = \sigma\langle S^z\rangle \{ E^{(d)}_J(q) + E^{(s)}_J(q) \} - \{ E(q) - E_W(q)\} \Delta n^{-\sigma(d)}_q -$$

$$- N(q)\{ \Omega^{-\sigma}_q(T) + \Omega^{-\sigma}_q(V)\} \qquad (36)$$

2º) Determination of $\Omega^{\sigma}_q(V)$

Introduce the new "susceptibilities":

$$\chi_2(k,q) = \frac{1}{2\pi} F_\omega \{g_{k+q}(\omega)\, \frac{1}{\omega - \varepsilon^{(s)}_{k+q}}\, g_k(\omega)\}$$

$$\tilde{\chi}_2(k,q) = \frac{1}{2\pi} F_\omega \{g_{k+q}(\omega)\, \frac{\omega}{\omega - \varepsilon^{(s)}_{k+q}}\, g_k(\omega)\}$$

$$\chi_3(k,q) = \frac{1}{2\pi} F_\omega \{g_{k+q}(\omega)\frac{1}{(\omega-\varepsilon^{(s)}_{k+q})^2}\, \frac{1}{\omega-\varepsilon^{(s)}_k}\, g_k(\omega)\}$$

$$\chi_4(k,q) = \frac{1}{2\pi} F_\omega \{ \frac{1}{(\omega-\varepsilon^{(s)}_{k+q})(\omega-\varepsilon^{(s)}_k)} g_k(\omega)\} \qquad (37\text{-a})$$

Using (37-a) one gets from (33-b):

$$\Omega^{\sigma}(V) = \langle S^{z}\rangle\sigma \{ |V_{sd}|^2 \sum_k J^{(R)}_{eff}(k+q,k)\ \chi_2(k,q) +$$

$$+ |V_{sd}|^4 (\bar{n}^{(d)})^2 \sum_k J^{(s)}(k+q,k)\ \chi_3(k,q) +$$

$$+ |V_{sd}|^2\ \bar{n}^{(d)} \sum_k J^{(s)}(k+q,k)\chi_4(k,q)\} - \Delta n_q^{-\sigma(d)}\{|V_{sd}|^2 \sum_k \tilde{\chi}_2(k,q)$$

$$- |V_{sd}|^2 \langle n^{(d)}\rangle \sum_k \left[\tilde{W}^{(o)}_{k+q} + \tilde{W}^{(o)}_{k}\right] \chi_2(k,q)\} - |V_{sd}|^2 \sum_k \chi_2(k,q)\{ \Omega_q^{-\sigma}(T) +$$

$$+ \Omega_q^{-\sigma}(V)\} \qquad (37\text{-b})$$

Again we introduce new definitions like:

$$E^{J_d}_{sd}(q) = |V_{sd}|^2 \sum_k J^{(R)}_{eff}(k+q,k)\ \chi_2(k,q)$$

$$E^{J_s}_{sd}(q) = |V_{sd}|^2\ \bar{n}^{(d)} \sum_k J^{(s)}(k+q,k)\ \chi_4(k,q) + |V_{sd}|^4 (\bar{n}^{(d)})^2 \sum_k J^{(s)}(k+q,k)\chi_3(k,q)$$

$$E^{(d)}_{sd} = |V_{sd}|^2 \sum_k \tilde{\chi}_2(k,q)$$

$$E^{W}_{sd}(q) = |V_{sd}|^2 \langle n^{(d)}\rangle \sum_k (\tilde{W}^{(o)}_{k+q} + \tilde{W}^{(o)}_{k})\ \chi_2(k,q) \qquad (37\text{-c})$$

and the "ocupation number":

$$N_{sd}^{(d)}(q) = |V_{sd}|^2 \sum_k \chi_2(k,q) \qquad (37\text{-d})$$

In terms of these quantities:

$$\Omega_q^{\sigma}(V) = \langle S^z\rangle\sigma \{ E_{sd}^{J_d}(q) + E_{sd}^{J_s}(q)\} - \Delta n_q^{-\sigma(d)} \{E_{sd}^{(d)}(q) - E_{sd}^{(w)}(q) \} -$$

$$- N_{sd}^{(d)}(q) \{ \Omega_q^{-\sigma}(T) + \Omega_q^{-\sigma}(V) \} \qquad (38)$$

39) Solution of the coupled equations (36) and (38)

Since the equation of motion (33-a) for $G_{kk'}^{11(1)}$ only involves $\Omega_q^{-\sigma}(T) + \Omega_q^{-\sigma}(V)$ we firstly add equations (36) and (38) to get:

$$\Omega_q^{\sigma} = \langle S^z\rangle\sigma \{ E_{eff}^{J(s)}(q) + E_{eff}^{J(s)}(q)\} - \Delta n_q^{-\sigma(d)} E_{eff}^{(d)}(q) -$$

$$- \Omega_q^{-\sigma} N_{eff}^{(d)}(q) \qquad (39\text{-a})$$

where we have defined:

$$\Omega_q^{\sigma} = \Omega_q^{\sigma}(T) + \Omega_q^{\sigma}(V)$$

cont.

$$E^{Jd}_{eff}(q) = E^{(d)}_{J}(q) + E^{Jd}_{sd}(q)$$

$$E^{Js}_{eff}(q) = E^{(s)}_{J}(q) + E^{Js}_{sd}(q)$$

$$E^{(d)}_{eff}(q) = E(q) + E^{(d)}_{sd}(q) - E^{(w)}(q) - E^{(w)}_{sd}(q)$$

$$N^{(d)}_{eff}(q) = N(q) + N^{(d)}_{sd}(q) \tag{39-b}$$

Equation (39-a) has the following solution (changing σ to $-\sigma$ and solving the coupled system):

$$\Omega^{-\sigma}_{q} = \langle S^{z}\rangle\sigma \; \frac{E^{J_d}_{eff}(q) + E^{J_s}_{eff}(q)}{1 - N^{(d)}_{eff}(q)} + \frac{\Delta n^{-\sigma(d)}_{q} E^{(d)}_{eff}(q) N^{(d)}_{eff}(q) - \Delta n^{\sigma(d)}_{q} E^{(d)}_{eff}(q)}{1 - \left[N^{(d)}_{eff}(q)\right]^{2}} \tag{40}$$

d) *Self-consistent determination of* $\Delta n^{\sigma(d)}_{q}$

Now we return to equation (33-a) and use the prescription:

$$\Delta n^{\sigma(d)}_{q} = \sum_{k} F_{\omega}\left[G^{11(1)}_{k+q,k;\sigma}(\omega) \right]$$

to obtain:

$$\Delta n^{\sigma(d)}_{q} = \sigma\langle S^{z}\rangle \left[\chi^{(d)}_{(J)}(q) + \chi^{(s)}_{(J)}(q) \right] - \Delta n^{-\sigma(d)}_{q} \left[N_{1}(q) - N_{w}(q)\right] - \Omega^{-\sigma}\chi_{o}(q) \tag{41-a}$$

where we have defined:

$$\chi^{(d)}_{(J)}(q) = \sum_k J^{(R)}_{eff}(k+q,k)\ \chi_1(k,q)$$

$$\chi^{(s)}_{(J)}(q) = (n^{(d)})^2\ |V_{sd}|^2\ \sum_k J^{(s)}(k+q,k)\ \chi(k,q)$$

$$N_1(q) = \sum_k \tilde{\chi}_1(k,q)$$

$$N_w(q) = \sum_k \langle n^{(d)}\rangle\ \{\tilde{W}^{(o)}_{k+q} + \tilde{W}^{(o)}_k\}\ \chi_1(k,q)$$

$$\chi_o(q) = \sum_k \chi_1(k,q) \qquad (41\text{-b})$$

Combining equations (41-a) and (40) and solving for $\Delta n^{\sigma(d)}_q$ one obtains the final result:

$$\Delta n^{\sigma(d)}_q = \langle S^z\rangle\sigma \sum_{i=s,d} \frac{\chi^{(i)}_{(J)}(q)\ \{1-N^{(d)}_{eff}(q) + E^{J(i)}_{eff}(q)\chi_o(q)}{\{\ 1-\left[N_1(q)-N_w(q)\right]\ \{1-N^{(d)}_{eff}(q) - \dfrac{E^{(d)}_{eff}(q)\chi_o(q)}{1-(N_1(q)-N_w(q))}\ \}} \qquad (42)$$

III) FINAL RESULTS AND DISCUSSION

Equation (42) suggests that the d-electron magnetization ($m^{(d)}_q = n^{(d)}_q - n^{-\sigma(d)}_q$) induced by the local moment, has two different contributions. One due to the direct local moment - d-electron effective coupling $J^{(R)}_{eff}$, and the other due to $J^{(s)}$. The last contribution comes from the fact that the s and d bands are coupled through V_{sd} mixing. In this way we can write the d-magnetization in terms of "partial susceptibilities":

$$m^{(d)}_q = 2 \langle S^z \rangle \{\sum_k J^{(R)}_{eff}(k+q,k)\ \chi^{dd}(k,q) + \sum_k J^{(s)}(k+q,k)\chi^{ds}(k,q)\} \tag{43}$$

where we have defined:

$$\chi^{dd}(k,q) = \frac{1}{D(q)}\ \chi_1(k,q)\left[1-N^{(d)}_{eff}(q)\right] + \chi_o(q)\left[\varepsilon^{(d)}_{k+q}\chi_1(k,q) + |V_{sd}|^2\chi_2(k,q)\right] \tag{44-a}$$

$$\chi^{ds}(k,q) = \frac{|V_{sd}|^2}{D(q)}\left\{(\bar{n}^{(d)})^2\chi(k,q)\left[1-N^{(d)}_{eff}(q)\right] + \chi_o(q)\left[(n^{(d)})^2\varepsilon^{(d)}_{k+q}\chi(k,q) + \bar{n}^{(d)}\chi_4(k,q) + |V_{sd}|^2(\bar{n}^{(d)})^2\chi_3(k,q)\right]\right\} \tag{44-b}$$

where the denominator is:

$$D(q) = \{1 - \left[N_1(q) - N_W(q)\right]\}\{1 - N^{(d)}_{eff}(q)\} - E^{(d)}_{eff}(q)\chi_o(q) \tag{44-c}$$

Equation (43) has the same form of the previously obtained results derived within the Hartree-Fock [1] , [2] and Hubbard [3] approach. One should note that the "partial susceptibilities" $\chi^{dd}(k,q)$ and $\chi^{ds}(k,q)$ have the same poles, given by $D(q) = 0$, but diferentes residues.

When the exchange couplings can be approximated by q-dependent functions ($J(k+q;k) = J(q)$) the "effective d-coupling" $J^{(R)}_{eff}(k+q;k)$ reduces also to q-dependent function:

$$J^{(R)}_{eff}(q) = J^{(d)}\{ n^{(d)} + \sum_{q'} [<P_{q'}> - <Q_{q'}>] \} \qquad (45\text{-a})$$

where:

$$<P_{q'}> = \sum_{i,j} \ell^{iq'(R_i-R_j)} \{ <n^{(d)}_{i-\sigma} n^{(d)}_{j-\sigma}>^{(o)} - <[d^{+}_{i-\sigma} d_{j-\sigma} + d^{+}_{j-\sigma} d_{i-\sigma}] d^{+}_{j\sigma} d_{i\sigma}>^{(o)} \} \qquad (45\text{-b})$$

$$<Q_{q'}> = \sum_{i,j} \ell^{iq'(R_i-R_j)} \{ <d^{+}_{j-\sigma} d_{i-\sigma}>^{(o)} - <n^{(d)}_{i\sigma} d^{+}_{j-\sigma} d_{i-\sigma}>^{(o)} - - <n^{(d)}_{i\sigma} d^{+}_{i-\sigma} d_{j-\sigma}>^{(o)} \} \qquad (45\text{-c})$$

In this situation the magnetization assumes the following form:

$$m^{(d)}_{q} = 2<S^{z}>\{ J^{R}_{eff}(q) \chi^{dd}(q) + J^{(s)}(q) \chi^{ds}(q) \} \qquad (46)$$

Finally we neglect the s-d mixing in order to discuss a single strongly correlated band. Then $\chi^{ds}_{(q)} = 0$, and the d-magnetization can be writen in sipler way. In fact using (41-b), (39-b) and (35-c) one gets:

$$\sum_k \{ \chi_1(k,q) \ [\ 1-N(q)\ ] + \epsilon^{(d)}_{k+q}\ \chi_1(k,q)\ \chi_o(q)\} = \chi_o(q)\ [1-N(q)] +$$

$$+ N(q)\ \chi_o(q) = \chi_o(q) \qquad (47\text{-a})$$

Then:

$$m^{(d)}_q = 2 <S^z> J^{(R)}_{eff}(q)\ \chi^{(d)}(q) \qquad (47\text{-b})$$

where $\chi^{(d)}(q) = \dfrac{\chi_o(q)}{D(q)}$, and $D(q)$ reduces to:

$$D(q) = \{ 1 - [N_1(q) - N_W(q)] \}\ \{1 - N(q)\} - \{ E(q) - E^W(q)\}\ \chi_o(q)$$

which is, appart from a constant term in the denominator, the same result obtained by Schweitzer [7].

APPENDIX A

COMPARISON TO HUBBARD'S APPROACH

We start transforming equation (24-a):

$$G_{kk'}^{11(1)}(\omega) = \frac{1}{2\pi} g_k(\omega)\, J_{eff}^{(H)}(k,k')\, \langle S^z\rangle\sigma\, g_{k'}(\omega) +$$

$$+ \frac{1}{2\pi} g_k(\omega)\, V_{ds} \frac{1}{\omega-\varepsilon_k^{(s)}} (\overline{n}^{(d)})^2\, J^{(s)}(k,k')\, \langle S^z\rangle\sigma \frac{1}{\omega-\varepsilon_k^{(s)}} V_{sd}\, g_{k'}(\omega)$$

$$- \frac{1}{2\pi} g_k(\omega)\, \omega\, \Delta n_{kk'}^{-\sigma(d)} g_{k'}(\omega) + \frac{1}{2\pi} g_k(\omega) \{ M_{kk'}^{\sigma} + K_{kk'}^{\sigma} (J^{(d)}) +$$

$$+ \langle n^{(d)}\rangle^2 \left[\sum_{k''} J^{(d)}(k'',k''+k-k') - J^{(d)}(k,k')\right] \langle S^z\rangle\sigma \}\, g_{k'}(\omega) \qquad \text{(A-1)}$$

where we defined the Hubbard "effective exchange" [3] as:

$$J_{eff}^{(H)}(k,k') = \overline{n}^{(d)} \left[J^{(d)}(k,k') + \langle n^{(d)}\rangle \{ \sum_{k''} J^{(d)}(k'',k''+k-k') - J^{(d)}(k,k')\}\right] \qquad \text{(A-2)}$$

The last term of (A-1) is rewritten as:

$$- \frac{1}{2\pi} g_k(\omega)\, \overline{n}^{(d)}\, \alpha_{kk'}^{-\sigma(1)} + \frac{1}{2\pi} g_k(\omega) \{ \overline{M}_{kk'}^{\sigma} + K_{kk'}^{\sigma} (J^{(d)}) +$$

$$+ \langle n^{(d)}\rangle^2 \left[\sum_{k''} J^{(d)}(k'',k''+k-k') - J^{(d)}(k,k') \right] \langle S^z\rangle\sigma \}\; g_{k'}(\omega) \qquad \text{(A-3)}$$

$\overline{M}_{kk'}$ being defined as:

$$\overline{M}^{\sigma}_{kk'} = \Big[\tilde{\Lambda}^{(1)\sigma}_{ij} - \langle n^{(d)}\rangle \{ \Delta n^{(d)}_{i-\sigma} + \Delta n^{(d)}_{j-\sigma} \} T^{(d)}_{ij} + \langle n^{(d)}\rangle \{ \Delta n^{(d)}_{i-\sigma} + $$

$$+ \Delta n^{(d)}_{j-\sigma} \} \tilde{W}^{(o)}_{ij} - \langle n^{(d)}\rangle \alpha^{(1)}_{i-\sigma} \delta_{ij}\Big]_{kk'} \qquad \text{(A-4)}$$

Expressions (A-3) and (A-4) are now transformed to give:

$$X_{kk'} = K^{\sigma}_{kk'}(J^{(d)}) + \langle n^{(d)}\rangle^2 \Big[\sum_{k''} J^{(d)}(k'',k''+k-k') - J^{(d)}(k,k')\Big] \langle S^z\rangle\sigma$$

$$= \Big[K^{\sigma}_{ij}(J^{(d)}) + \langle n^{(d)}\rangle^2 \Big[J^{(d)}(R_i,R_i)\,\delta_{ij} - J^{(d)}(R_i,R_j)\Big] \langle S^z\rangle\sigma\Big]_{kk'}$$

$$= \Big[K^{\sigma}_{ij}(J^{(d)}) - \langle n^{(d)}\rangle^2 J^{(d)}(R_i,R_j) \langle S^z\rangle\sigma + $$

$$+ \langle n^{(d)}\rangle^2 J^{(d)}(R_i,R_i)\,\delta_{ij} \langle S^z\rangle\sigma\Big]_{kk'}$$

Using equation (12-b) and excluding the i=l terms in the last term of this equation, one gets (in the infinite repulsion limit):

$$X_{ij}(J^{(d)}) = \overline{K}^{\sigma}_{ij}(J^{(d)}) - \langle n^{(d)}\rangle^2 J^{(d)}(R_i,R_j) \langle S^z\rangle\sigma - $$

$$- \langle n^{(d)}\rangle (1 - \langle n^{(d)}\rangle)\,\delta_{ij}\, J^{(d)}(R_i,R_i) \langle S^z\rangle\,\sigma \qquad \text{(A-5)}$$

where the bar emphasizes that only terms whith $i \neq l$ in (12-b) are included in $\overline{K}_{ij}$. An exchange "band shift" $W_{ij}(J^{(d)})$ is now defined as: (The definition is suggested by expression 13-a):

$$\langle n^{(d)}\rangle(1 - \langle n^{(d)}\rangle)W^{\sigma}_{ij}(J^{(d)}) = \bar{K}^{\sigma}_{ij}(J^{(d)}) - \langle n^{(d)}\rangle^{2}\ J^{(d)}(R_i,R_j)\ \langle S^z\rangle\sigma -$$

$$- \langle n^{(d)}\rangle(1 - \langle n^{(d)}\rangle)J^{(d)}(R_i,R_i)\langle S^z\rangle\sigma\ \delta_{ij} \tag{A-6}$$

Now we transform the expression (A-4); from equation (13-a) one gets:

$$\tilde{\Lambda}^{(1)}_{ij} = \langle n^{(d)}\rangle(1 - \langle n^{(d)}\rangle)\tilde{W}^{(1)}_{ij} + \langle n^{(d)}\rangle\{\Delta n^{(d)}_{i-\sigma} + \Delta n^{(d)}_{j-\sigma}\}T^{(d)}_{ij} -$$

$$- \langle n^{(d)}\rangle\ \{\Delta n^{(d)}_{i-\sigma} + \Delta n^{(d)}_{j-\sigma}\}\tilde{W}^{(1)}_{ij} + \Delta n^{(d)}_{i-\sigma}\ \tilde{W}^{(d)}_{ij} + \langle n^{(d)}\rangle\alpha^{(1)}_{i-\sigma}\ \delta_{ij} \tag{A-7}$$

Using (A-7) one sees that $\bar{M}_{ij}$ given by (A-4) may be rewritten as:

$$\bar{M}_{ij} = \langle n^{(d)}\rangle\ (1-\langle n^{(d)}\rangle)\tilde{W}^{(1)}_{ij} + \Delta n^{(d)}_{i-\sigma}\ \tilde{W}^{(o)}_{ij} = \langle n^{(d)}\rangle(1 - \langle n^{(d)}\rangle)\tilde{W}^{(1)}_{ij} +$$

$$+ \bar{n}^{(d)}\ \tilde{W}^{(o)}_{ij}\ \Delta n^{(d)}_{i-\sigma} + \langle n^{(d)}\rangle\ \tilde{W}^{(d)}_{ij}\ \Delta n^{(d)}_{i-\sigma} \tag{A-8}$$

Substituing (A-8), (A-6) in equation (A-1) one gets:

$$G^{11(1)}_{kk'}(\omega) = \frac{1}{2\pi}\ g_k(\omega)\ J^{(H)}_{eff}(k,k')\ \langle S^z\rangle\sigma\ g_{k'}(\omega) +$$

$$+ \frac{1}{2\pi}\ g_k(\omega)\ V_{ds}\ \frac{1}{\omega-\varepsilon^{(s)}_{k}}\ (\bar{n}^{(d)})^{2}\ J^{(s)}(k,k')\langle S^z\rangle\sigma\ \frac{1}{\omega-\varepsilon^{(s)}_{k'}}\ V_{sd}\ g_{k'}(\omega) -$$

$$- \frac{1}{2\pi}\ g_k(\omega)\{\ \omega-\langle n^{(d)}\rangle\ \tilde{W}^{(o)}_{k}\}\ g_{k'}(\omega) - \frac{1}{2\pi}\ g_k(\omega)\ \bar{n}^{(d)}\ \alpha^{-\sigma}_{kk'}\ g_{k'}(\omega) +$$

cont.

$$+ \frac{1}{2\pi} g_k(\omega) \overline{n}^{(d)} \{ <n^{(d)}> W_{kk'}(J^{(d)}) + \tilde{W}_{k'}^{(o)} \Delta n_{kk'}^{-\sigma(d)} + <n^{(d)}> \tilde{W}_{kk'}^{(1)\sigma} \} g_{k'}(\omega)$$

(A-9)

Now if band shift effects are neglected in (A- 9) both explicitly and in the propagators one recovers the Hubbard result obtained previously.

APPENDIX B

PROPAGATORS $G_{kk'}^{21(1)}(\omega)$, $G_{kk'}^{12(1)}(\omega)$, $G_{kk'}^{S2(1)}(\omega)$ and $G_{kk'}^{2S(1)}(\omega)$ IN THE INFINITE REPULSION LIMIT

From equation (22-c) and using the fact that propagators $G_{kk'}^{11(1)}(\omega)$, $G_{kk'}^{S1(1)}(\omega)$ and $g_{k'}(\omega)$ are finite and $g_k^{21(0)}(\omega)$ is zero one gets for $I \to \infty$:

$$\lim_{I \to \infty} G_{kk'}^{21(1)}(\omega) = 0 \qquad \text{(B-1)}$$

Now we firstly discuss the propagator $G_{kk'}^{S2(1)}(\omega)$. Using equations (6), (9-b), (14-b), (15) and (17-a) one obtains the following first order coupled equations of motion:

$$\omega G_{ij}^{S2(1)}(\omega) - \sum_{\ell} T_{i\ell}^{(s)} G_{\ell j}^{S2(1)}(\omega) - V_{sd} G_{ij}^{12(1)}(\omega) =$$

$$= \sum_{\ell} J^{(s)}(R_i, R_\ell) <S^z> \sigma G_{\ell j}^{S2(o)}(\omega) \qquad \text{(B-2a)}$$

$$\omega\, G_{ij}^{12(1)}(\omega) - \sum_{\ell} T_{i\ell}^{(d)}\, G_{\ell j}^{12(1)}(\omega) - V_{sd}\, G_{ij}^{S2(1)}(\omega) - I\, G_{ij}^{22(1)}(\omega) =$$

$$= \Delta n_{i-\sigma}^{(d)}\, \delta_{ij} + \sum_{\ell} J^{(d)}(R_i, R_\ell)\, \langle S^z \rangle \sigma\, G_{j}^{12(0)}(\omega) \qquad \text{(B-2b)}$$

$$(\omega - I) G_{ij}^{22(1)}(\omega) - \sum_{\ell} \tilde{W}_{i\ell}^{(0)} G_{\ell j}^{22(1)}(\omega) - \langle n^{(d)} \rangle \sum_{\ell} (T_{i\ell}^{(d)} - \tilde{W}_{i\ell}^{(0)}) G_{\ell j}^{12(1)}(\omega) -$$

$$- \langle n^{(d)} \rangle V_{ds}\, G_{ij}^{S2(1)}(\omega) = \Delta n_{i-\sigma}^{(d)}\, \delta_{ij} + \Delta n_{i-\sigma}^{(d)}\, V_{ds}\, G_{ij}^{S2(0)}(\omega) +$$

$$+ \sum_{\ell} A_{i\ell}^{\sigma}\, G_{\ell j}^{12(0)}(\omega) + \sum_{\ell} B_{i\ell}^{\sigma}\, G_{\ell j}^{22(0)}(\omega) \qquad \text{(B-2c)}$$

Quite similarly one gets for the zero-order propagators:

$$\omega\, G_{ij}^{S2(0)}(\omega) - \sum_{\ell} T_{i\ell}^{(s)}\, G_{\ell j}^{S1(0)}(\omega) - V_{sd}\, G_{ij}^{12(0)}(\omega) = 0 \qquad \text{(B-3a)}$$

$$\omega\, G_{ij}^{12(0)}(\omega) - \sum_{\ell} T_{i\ell}^{(d)}\, G_{\ell j}^{12(0)}(\omega) - V_{sd}\, G_{ij}^{S2(0)}(\omega) - I\, G_{ij}^{22(0)}(\omega) = \langle n^{(d)} \rangle \delta_{ij} \qquad \text{(B-3b)}$$

$$(\omega - I) G_{ij}^{22(0)}(\omega) - \sum_{\ell} \tilde{W}_{i\ell}^{(0)}\, G_{\ell j}^{22(0)}(\omega) - \langle n^{(d)} \rangle \sum_{\ell} (T_{i\ell}^{(d)} - \tilde{W}_{i\ell}^{(0)}) G_{\ell j}^{12(0)}(\omega) -$$

$$- \langle n^{(d)} \rangle V_{ds}\, G_{ij}^{S2(0)}(\omega) = \langle n^{(d)} \rangle\, \delta_{ij} \qquad \text{(B-3c)}$$

Now Fourier transforming equations (B-3):

$$(\omega-\varepsilon_k^{(s)})G_{kk'}^{s2(o)}(\omega) = V_{sd}\ G_{kk'}^{12(o)}(\omega) \qquad \text{(B-4a)}$$

$$(\omega-\varepsilon_k^{(d)})G_{kk'}^{12(o)}(\omega) = \langle n^{(d)}\rangle\ \delta_{kk'} + I\ G_{kk'}^{22(o)}(\omega) + V_{sd}\ G_{kk'}^{s2(o)}(\omega) \qquad \text{(B-4b)}$$

$$(\omega-I-\tilde{W}_k^{(o)})G_{kk'}^{22(o)}(\omega) = \langle n^{(d)}\rangle\ \delta_{kk'} + \langle n^{(d)}\rangle(\varepsilon_k^{(d)}-\tilde{W}_k^{(o)})G_{kk'}^{12(o)}(\omega) +$$

$$+ \langle n^{(d)}\rangle V_{ds}\ G_{kk'}^{s2(o)}(\omega) \qquad \text{(B-4c)}$$

In the infinite repulsion limit:

$$IG_{kk'}^{22(o)}(\omega) = -\ \langle n^{(d)}\rangle\ \delta_{kk'} - \langle n^{(d)}\rangle\ (\varepsilon_k^{(d)}-\tilde{W}_k^{(o)})G_{kk'}^{12(o)}(\omega) -$$

$$- \langle n^{(d)}\rangle\ V_{ds}\ G_{kk'}^{s2(o)}(\omega)$$

So equation (B-4b) becomes:

$$\{\ \omega-\ \overline{n}^{(d)}\tilde{\varepsilon}_k^{(d)} - \langle n^{(d)}\rangle\ \tilde{W}_k^{(o)}\ \}G_{kk'}^{12(o)}(\omega) = 0 \quad \text{or} \quad G_{kk'}^{12(o)}=0 \qquad \text{(B-5)}$$

where we used equation (B-4a) for $G_{kk'}^{s2(0)}(\omega)$.

Consequently:

$$\lim_{I \to \infty} G_{kk'}^{22(o)}(\omega) = \lim_{I \to \infty} G_{kk'}^{12(o)}(\omega) = \lim_{I \to \infty} G_{kk'}^{s2(o)}(\omega) = 0 \qquad \text{(B-6)}$$

Now returning to equations (B-2) one gets:

$$(\omega-\varepsilon_k^{(s)})G_{kk'}^{s2(1)}(\omega) = V_{sd}\, G_{kk'}^{12(1)}(\omega)$$

$$(\omega-\varepsilon_k^{(d)})G_{kk'}^{12(1)}(\omega) = \Delta n_{kk'}^{-\sigma(d)} + I\, G_{kk'}^{22(1)}(\omega) + V_{sd}\, G_{kk'}^{s2(1)}(\omega)$$

$$(\omega-I-\tilde{W}_k^{(o)})G_{kk'}^{22(1)}(\omega) = \Delta n_{kk'}^{-\sigma(d)} + \langle n^{(d)}\rangle(\varepsilon_k^{(d)}-\tilde{W}_k^{(o)})G_{kk'}^{12(1)}(\omega) +$$

$$+ \langle n^{(d)}\rangle\, V_{ds}\, G_{kk'}^{s2(1)}(\omega) \qquad \text{(B-7)}$$

where we neglected the zero-order propagator since we know they vanish in the infinite repulsion limit. The coupled system (B-7) is formally identical to (B-4); then one gets:

$$\lim_{I \to \infty} G_{kk'}^{22(1)}(\omega) = \lim_{I \to \infty} G_{kk'}^{12(1)}(\omega) = \lim_{I \to \infty} G_{kk'}^{s2(1)}(\omega) = 0 \qquad \text{(B-8)}$$

Finally, using the same procedure, one obtain the following coupled equations involving the $G_{ij}^{2s(1)}(\omega)$ propagator:

$$\omega\, G_{ij}^{ss(1)}(\omega) - \sum_{\ell} T_{i\ell}^{(s)}\, G_{\ell j}^{ss(1)}(\omega) - V_{sd}\, G_{ij}^{1s(1)}(\omega) = \sum_{\ell} J^{(s)}(R_i,R_\ell)\langle S^z\rangle\sigma\, G_{\ell j}^{ss(o)}(\omega)$$

(B-9a)

$$g_k(\omega) = \frac{\omega - \varepsilon_k^{(s)}}{(\omega - \bar{n}^{(d)}\varepsilon_k^{(d)} - \langle n^{(d)}\rangle \tilde{W}_k^{(o)})(\omega - \varepsilon_k^{(s)}) - n^{(d)}|V_{sd}|^2} \tag{C-1}$$

since the denominator provides a second degree equation which solutions $E_k^{(1)}$ and $E_k^{(2)}$, the propagator $g_k(\omega)$ reads:

$$g_k(\omega) = \frac{\omega - \varepsilon_k^{(s)}}{(\omega - E_k^{(1)})(\omega - E_k^{(2)})} \tag{C-2}$$

Using this expression for $g_k(\omega)$, the "susceptibilities" (34) and (37-a) become:

$$\chi_1(k,q) = \frac{1}{2\pi} F_\omega \left\{ \frac{(\omega-\varepsilon_{k+q}^{(s)})(\omega-E_k^{(s)})}{(\omega-E_{k+q}^{(1)})(\omega-E_{k+q}^{(2)})(\omega-E_k^{(1)})(\omega-E_k^{(2)})} \right\}$$

$$\tilde{\chi}_1(k,q) = \frac{1}{2\pi} F_\omega \left\{ \frac{\omega(\omega-\varepsilon_{k+q}^{(s)})(\omega-\varepsilon_k^{(s)})}{(\omega-E_{k+q}^{(1)})(\omega-E_{k+q}^{(2)})(\omega-E_k^{(1)})(\omega-E_k^{(2)})} \right\}$$

$$\chi(k,q) = \frac{1}{2\pi} F_\omega \left\{ \frac{1}{(\omega-E_{k+q}^{(1)})(\omega-E_{k+q}^{(2)})(\omega-E_k^{(1)})(\omega-E_k^{(2)})} \right\}$$

$$I\ G^{2s(1)}_{kk'}(\omega) = - \langle n^{(d)}\rangle(\varepsilon^{(d)}_k - \tilde{W}^{(o)}_k) G^{1s(1)}_{kk'}(\omega) - \langle n^{(d)}\rangle V_{ds}\ G^{ss(1)}_{kk'}(\omega) -$$

$$- \Delta n^{-\sigma(d)}_{kk'} V_{ds}\ G^{ss(o)}_{k'}(\omega) - A^{\sigma}_{kk'} G^{1s(o)}_{k'}(\omega) - B^{\sigma}_{kk'}\ G^{2s(o)}_{k'}(\omega) \qquad \text{(B-11)}$$

Substituing (B-11) in (B-10b) and solving the coupled equations (B-10a) and (B-10b) one gets:

$$\left\{ \omega - \varepsilon^{(s)}_k - \frac{\bar{n}^{(d)}|V_{sd}|^2}{\omega - \varepsilon^{(d)}_k \bar{n}^{(d)} - \langle n^{(d)}\rangle \tilde{W}^{(o)}_k} \right\} G^{ss(1)}_{kk'}(\omega) = J^{(s)}(k,k')\langle S^z\rangle\sigma\ G^{ss(o)}_{k'}(\omega) +$$

$$+ \frac{V_{sd}}{\omega - \bar{n}^{(d)}\varepsilon^{(d)}_k - \langle n^{(d)}\rangle\ \tilde{W}^{(o)}_k} \left\{ J^{(d)}(k,k')\langle S^z\rangle\sigma\ G^{1s(o)}_{k'}(\omega) - \right.$$

$$\left. - \Delta n^{-\sigma(d)}_{kk'} V_{ds}\ G^{ss(o)}_{k'}(\omega) - A^{\sigma}_{kk'}\ G^{1s(o)}_{k'}(\omega) - B^{\sigma}_{kk'}\ G^{2s(o)}_{k'}(\omega) \right\} \qquad \text{(B-12)}$$

From this equation, since that the zero order propagators involved are finite [10], one sees that $G^{ss(1)}_{kk'}(\omega)$ is finite in this limit and from (B-10a) that the $G^{1s(1)}_{kk'}(\omega)$ is also finite. Now we conclude, from (B-10c) that the propagator $G^{2s(1)}_{kk'}(\omega)$ vanish in the infinite repulsion limit.

APPENDIX C

EXPLICIT FORM OF THE "SUSCEPTIBILITIES"

We start rewriting the zero order propagator in more convenient way. From equations (21) one gets:

$$g_k(\omega) = \frac{\omega - \varepsilon_k^{(s)}}{(\omega - \overline{n}^{(d)}\varepsilon_k^{(d)} - \langle n^{(d)}\rangle \tilde{W}_k^{(o)})(\omega - \varepsilon_k^{(s)}) - n^{(d)}|V_{sd}|^2} \tag{C-1}$$

since the denominator provides a second degree equation which solutions $E_k^{(1)}$ and $E_k^{(2)}$, the propagator $g_k(\omega)$ reads:

$$g_k(\omega) = \frac{\omega - \varepsilon_k^{(s)}}{(\omega - E_k^{(1)})(\omega - E_k^{(2)})} \tag{C-2}$$

Using this expression for $g_k(\omega)$, the "susceptibilities" (34) and (37-a) become:

$$\chi_1(k,q) = \frac{1}{2\pi} F_\omega \left\{ \frac{(\omega-\varepsilon_{k+q}^{(s)})(\omega-E_k^{(s)})}{(\omega-E_{k+q}^{(1)})(\omega-E_{k+q}^{(2)})(\omega-E_k^{(1)})(\omega-E_k^{(2)})} \right\}$$

$$\tilde{\chi}_1(k,q) = \frac{1}{2\pi} F_\omega \left\{ \frac{\omega(\omega-\varepsilon_{k+q}^{(s)})(\omega-\varepsilon_k^{(s)})}{(\omega-E_{k+q}^{(1)})(\omega-E_{k+q}^{(2)})(\omega-E_k^{(1)})(\omega-E_k^{(2)})} \right\}$$

$$\chi(k,q) = \frac{1}{2\pi} F_\omega \left\{ \frac{1}{(\omega-E_{k+q}^{(1)})(\omega-E_{k+q}^{(2)})(\omega-E_k^{(1)})(\omega-E_k^{(2)})} \right\}$$

$$\chi_2(k,q) = \frac{1}{2\pi} F_\omega \left\{ \frac{\omega - \varepsilon_k^{(s)}}{(\omega-E_{k+q}^{(1)})(\omega-E_{k+q}^{(2)})(\omega-E_k^{(1)})(\omega-E_k^{(2)})} \right\}$$

$$\tilde{\chi}_2(k,q) = \frac{1}{2\pi} F_\omega \left\{ \frac{\omega(\omega-\varepsilon_k^{(s)})}{(\omega-E_{k+q}^{(1)})(\omega-E_{k+q}^{(2)})(\omega-E_k^{(1)})(\omega-E_k^{(2)})} \right\}$$

$$\chi_3(k,q) = \frac{1}{2\pi} F_\omega \left\{ \frac{1}{(\omega-\varepsilon_{k+q}^{(s)})(\omega-E_{k+q}^{(1)})(\omega-E_{k+q}^{(2)})(\omega-E_k^{(1)})(\omega-E_k^{(2)})} \right\}$$

$$\chi_4(k,q) = \frac{1}{2\pi} F_\omega \left\{ \frac{1}{(\omega-\varepsilon_{k+q}^{(s)})(\omega-E_k^{(1)})(\omega-E_k^{(2)})} \right\} \qquad \text{(C-3)}$$

The final expressions for the "susceptibilities" are obtained using the identity:

$$\frac{1}{(\omega-E_{k+q}^{(\mu)})(\omega-E_k^{(\nu)})} = \frac{1}{E_{k+q}^{(\mu)}-E_k^{(\nu)}} \left\{ \frac{1}{\omega-E_{k+q}^{(\mu)}} - \frac{1}{\omega - E_k^{(\nu)}} \right\} \qquad \text{(C-4)}$$

and the property of the F_ω symbol:

$$F_\omega \left\{ \frac{n(\omega)}{\omega - E_k^{(\mu)}} \right\} = 2\pi\, n(E_k^{(\mu)})\, f(E_k^{(\mu)}) \qquad \text{(C-5)}$$

where the function $n(\omega)$ have no poles, and $f(\omega)$ is the Fermi-Dirac distribution. Then equations (C-3) have the explicit form:

$$\chi_1(k,q) = \sum_{\mu,\nu} (-1)^{\mu+\nu} \frac{(E^{(\mu)}_{k+q} - \varepsilon^{(s)}_{k+q})(E^{(\mu)}_{k+q} - \varepsilon^{(s)}_{k})f(E^{(\mu)}_{k+q})}{(E^{(1)}_{k+q} - E^{(2)}_{k})(E^{(1)}_{k} - E^{(2)}_{k})(E^{(\mu)}_{k+q} - E^{(\nu)}_{k})} - \frac{(E^{(\nu)}_{k} - \varepsilon^{(s)}_{k+q})(E^{(\nu)}_{k} - \varepsilon^{(s)}_{k})f(E^{(\nu)}_{k})}{(E^{(1)}_{k+q} - E^{(2)}_{k+q})(E^{(1)}_{k} - E^{(2)}_{k})(E^{(\mu)}_{k+q} - E^{(\nu)}_{k})}$$

$$\tilde{\chi}_1(k,q) = \sum_{\mu,\nu} (-1)^{\mu+\nu} \frac{E^{(\mu)}_{k+q}(E^{(\mu)}_{k+q} - \varepsilon^{(s)}_{k+q})(E^{(\mu)}_{k+q} - \varepsilon^{(s)}_{k})f(E^{(\mu)}_{k+q})}{(E^{(1)}_{k+q} - E^{(2)}_{k+q})(E^{(1)}_{k} - E^{(2)}_{k})(E^{(\mu)}_{k+q} - E^{(\nu)}_{k})} - \frac{E^{(\nu)}_{k}(E^{(\nu)}_{k} - \varepsilon^{(s)}_{k+q})(E^{(\nu)}_{k} - \varepsilon^{(s)}_{k})f(E^{(\nu)}_{k})}{(E^{(1)}_{k+q} - E^{(2)}_{k+q})(E^{(1)}_{k} - E^{(2)}_{k})(E^{(\mu)}_{k+q} - E^{(\nu)}_{k})}$$

$$\chi(k,q) \doteq \sum_{\mu,\nu} (-1)^{\mu+\nu} \frac{f(E^{(\mu)}_{k+q}) - f(E^{(\nu)}_{k})}{(E^{(1)}_{k+q} - E^{(2)}_{k+q})(E^{(1)}_{k} - E^{(2)}_{k})(E^{(\mu)}_{k+q} - E^{(\nu)}_{k})}$$

$$\chi_2(k,q) = \sum_{\mu,\nu} (-1)^{\mu+\nu} \frac{(E^{(\mu)}_{k+q}-\varepsilon^{(s)}_k)\; f(E^{(\mu)}_{k+q}) - (E^{(\nu)}_{k+q}-\varepsilon^{(s)}_k)\; f(E^{(\nu)}_k)}{(E^{(1)}_{k+q}-E^{(2)}_{k+q})(E^{(1)}_k-E^{(2)}_k)(E^{(\mu)}_{k+q}-E^{(\nu)}_k)}$$

$$\tilde{\chi}_2(k,q) = \sum_{\mu,\nu} (-1)^{\mu+\nu} \frac{E^{(\mu)}_{k+q}(E^{(\mu)}_{k+q}-\varepsilon^{(s)}_k)\; f(E^{(\mu)}_{k+q}) - E^{(\nu)}_k(E^{(\nu)}_k-\varepsilon^{(s)}_k) f(E^{(\nu)}_k)}{(E^{(1)}_{k+q}-E^{(2)}_{k+q})(E^{(1)}_k-E^{(2)}_k)(E^{(\mu)}_{k+q}-E^{(\nu)}_k)}$$

$$\chi_3(k,q) = \sum_{\mu,\nu} (-1)^{\mu+\nu} \frac{\alpha_{\mu\nu}(k,q)}{(E^{(1)}_{k+q} - E^{(2)}_{k+q})(E^{(1)}_k - E^{(2)}_k)(E^{(\mu)}_{k+q} - E^{(\nu)}_k)}$$

where

$$\alpha_{\mu\nu}(k,q) = \frac{f(\varepsilon^{(s)}_{k+q}) - f(E^{(\mu)}_{k+q})}{\varepsilon^{(s)}_{k+q} - E^{(\mu)}_{k+q}} - \frac{f(\varepsilon^{(s)}_{k+q} - f(E^{(\nu)}_k)}{\varepsilon^{(s)}_{k+q} - E^{(\nu)}_k}$$

$$\chi_4(k,q) = \frac{1}{E^{(s)}_{k+q} - E^{(2)}_k} \left\{ \frac{f(\varepsilon^{(s)}_{k+q})-f(E^{(1)}_k)}{{}^{(s)}_{k+q} - E^{(1)}_k} - \frac{f(\varepsilon^{(s)}_{k+q})-f(E^{(2)}_k)}{{}^{(s)}_{k+q} - E^{(2)}_k} \right\} \qquad \text{(C-6)}$$

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RÉSUMÉ

L'effet Mössbauer a permis de déceler, dans le système (Fe, Zn)SiF_6, $6H_2O$, la présence de deux types d'environnements pour l'ion ferreux, dont les proportions relatives varient avec la teneur en fer ainsi qu'avec la température entre 200 et 260 K. Par ailleurs, la diffraction de rayons X semble révéler, vers cette température, la formation d'une phase apparentée à $FeSiF_6$, $6H_2O$. Le champ cristallin auquel est soumis l'ion Fe^{2+} dépend de la température dans chacun des environnements.

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Les fluosilicates de fer et zinc, à température ambiante, ont pour groupes cristallins respectifs R$\bar{3}$m [1] et R$\bar{3}$ [2] ; les ions Fe^{2+} et Zn^{2+} occupent des sites octaédriques analogues. Un abaissement de symétrie vers 240 K a été observé dans le fluosilicate ferreux [3] mais il ne paraît pas affecter sensiblement la symétrie trigonale du champ cristallin agissant sur l'ion Fe^{2+} dont les propriétés magnétiques demeurent axiales à basse température [4].

1 - SPECTRES MÖSSBAUER DE POUDRES ET ETUDE AUX RAYONS X

Les spectres du fluosilicate de fer et du fluosilicate de zinc dopé au fer ont déjà été décrits [5,6]. Ils correspondent à des valeurs très différentes de l'interaction quadrupolaire (tableau 1). Les spectres des composés intermédiaires (fig. 1) résultent de la superposition de deux doublets de séparations respectives ΔE_{Q1} et ΔE_{Q2} correspondant approximativement aux doublets des échantillons de compositions extrêmes. Les valeurs ajustées de ΔE_{Q1} et ΔE_{Q2} à 300 K et 4,2 K ainsi que celles des proportions relatives des deux doublets, sont fournies dans le tableau 1. On constate que la répartition des ions Fe^{2+} entre les deux types d'environnements dépend de la teneur en fer et de la température. On a observé que la variation thermique de cette répartition dans les échantillons contenant 25% et 35% d'atomes de fer s'effectuait entre 200 et 260 K (températures croissantes) avec un hystérésis d'environ 20°.

TABLEAU 1 - Séparations quadrupolaires ΔE_{Q1} et ΔE_{Q2} en mm/s et intensités relatives correspondantes ajustées d'après les spectres Mössbauer à 300 et 4,2 K.

% Fe	ΔE_{Q1}, % (300 K)-		ΔE_{Q2}, % (300 K)		ΔE_{Q1}, % (4,2 K)		ΔE_{Q2}, % (4,2 K)	
2	1,88	100 %	-		1,92	100 %		
15	1,98	100 %	-		1,97	94 %	3,5	6 %
20	2,01	100 %	-		1,99	91 %	3,63	9 %
25	2,04	100 %	-		1,99	83 %	3,59	17 %
30	2,06	82 %	3,36	18 %	2,01	60 %	3,60	40 %
35	2,10	78 %	3,35	22 %	2,05	28 %	3,60	72 %
40	2,09	66 %	3,35	34 %	2,02	21 %	3,60	79 %
45	2,10	29 %	3,35	71 %	2,04	12 %	3,60	88 %
50	2,09	21 %	3,36	79 %	2,05	8 %	3,61	92 %
[illegible]	-		3,40	100 %	-		3,61	100 %

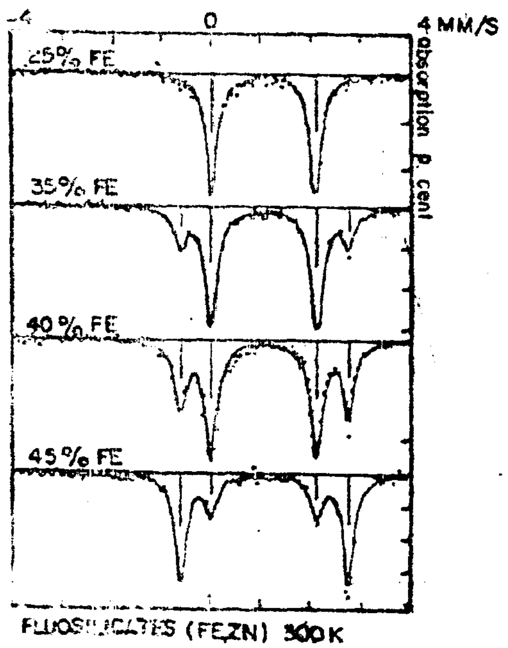

Figure 1

Spectres Mossbauer à 300 K pour diverses concentrations atomiques en fer.

L'étude par rayons X [7] du composé $ZnSiF_6$, $6H_2O$ n'a pas révélé de changement de phase cristalline entre 90 et 300°K, contrairement au cas de $FeSiF_6$, $6H_2O$. Les échantillons de fluosilicates mixtes contenant moins de 30 % d'atomes de fer présentent, à température ambiante, une phase cristalline unique dont les paramètres cristallins croissent régulièrement en fonction de la teneur en fer, le rapport $\frac{c}{a} \simeq 1,035$ (maille hexagonale) restant sensiblement constant. Au-delà de cette concentration en fer, les paramètres de la solution solide n'évoluent plus et il apparaît une deuxième phase apparentée à $FeSiF_6$, $6H_2O$ ($\frac{c}{a} \simeq 1,006$) dont la proportion croit avec la concentration globale en fer.

Il est remarquable que l'interaction quadrupolaire ΔE_{Q1} à température ambiante suive une loi du même type en fonction de la concentration en fer puisqu'une saturation intervient également à partir de la concentration de 35% (tableau 1). L'apparition d'un nouveau type d'environnement analogue à celui de $FeSiF_6$, $6H_2O$ semble toutefois détectable localement par l'effet Mössbauer avant que la phase correspondante ne soit visible par diffraction des rayons X. L'étude par rayons X de l'échantillon à 35 % de fer, en fonction de la température, montre que la proportion de la phase apparentée à $FeSiF_6$, $6H_2O$, à peine décelable à 300 K, augmente au-dessous de 240 K en même temps que sa symétrie est abaissée. La proportion accrue de cette phase es à rapprocher de l'augmentation de l'intensité du doublet correspondant dans les spectres Mössbauer. Comme il paraît difficile d'attribuer cette augmentation à la précipitation d'une phase plus riche en fer à aussi basse température, on est conduit à supposer un changement de symétrie cristalline transformant partiellement la solution solide en une phase semblable à celle de $FeSiF_6$, $6H_2O$ au-dessous de 240 K.

II - VARIATION THERMIQUE DU POTENTIEL CRISTALLIN TRIGONAL

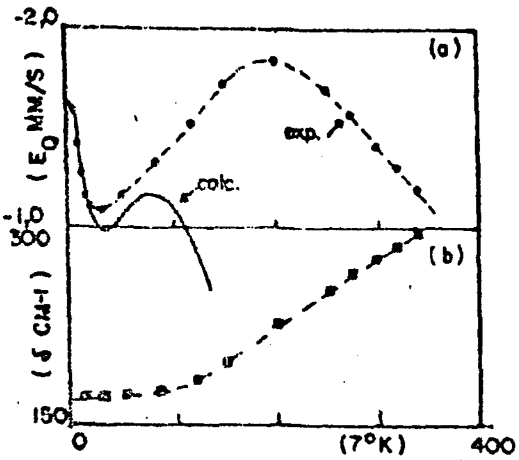

Figure 2

Variation thermique
a) de la séparation quadrupolaire ΔE_2,
b) du potentiel trigonal δ, dans le fluosilicate de zinc dopé en fer.

Le peuplement thermique des niveaux électroniques de l'ion ferreux est responsable de la variation thermique de l'interaction quadrupolaire $\Delta E_Q(T)$ généralement, on utilise la mesure de $\Delta E_Q(T)$ pour déterminer certaines caractéristiques du schéma de niveaux électroniques (méthode développé para Ingalls |8| dans un modèle de champ cristallin). Dans ces composés bien ioniques où les calculs de champ cristallin sont certainement valides, on observe avec surprise qu'il est impossible de rendre compte de $\Delta E_Q(T)$ dans la région de 1 à 300 K par une courbe de type Ingalls. Le cas du fluosilicate de Zn, dopé en Fe^{57}, est le plus démonstratif(fig. 2a): on a tracé une courbe de type Ingalls adaptée à la région des basses temperatures (1 à 15 K, voir|5|) qui manifestement ne convient pas pour les autres temperatures: il faut admettre que le potentiel trigonal (δ) dépend de la temperature (δ = écart entre niveaux orbitaux dû au potentiel trigonal); les valeurs δ(T), déduites de nos mesures, sont indiquées sur la figure 2b. Dans le fluosilicate ferreux, la dépendance thermique de δ a déjà été étudiée à partir de mesures magnétiques |9| ou des spectres Mössbauer |6| .

L'étude détaillé de l'interaction quadrupolaire, que nous avons faite dans $FeSiF_6$, $6H_2O$, n'a pas permis de détecter d'anomalie au voisinage de la température de changement de phase de 240 K qui semble peu affecter les propriétés locales du champ cristallin au site du fer. Nous n'avons pas observé non plus d'anomalie à 195 K, ce qui paraît infirmer certaines conclusions antérieures sur l'influence des mouvements de protons sur le spectre Mössbauer |10, 11|. Dans les fluosilicates de fer et de zinc dopé en fer, le potentiel trigonal δ(T) varie donc de façon continue avec la température, probablement en raison de déformations progressives de l'octaèdre $Fe(H_2O)_6|^{2+}$ car les coefficients de dilatation de ces fluosilicates ne sont pas anormalement grands |7|. Dans les fluosilicates mixtes de fer et de zinc où le potentiel cristallin doit conserver également, en première approximation, sa symétrie trigonale, une variation brutale de δ(T) se produit lorsque l'ion ferreux passe d'un type d'environnement à l'autre vers 240 K.

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