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Charge transfers in complex transition metal alloys (Ti_2Fe)

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Abstract. We introduce a new Non-Orthogonal Tight-Binding model, for complex alloys, in which electronic structure is characterized by charge transfers. We give the analytic calculation of a charge transfer, in which overlapping two-center terms are rigorously taken into account. Then, we apply numerically this result to an approximant phase of a quasicrystal of Ti_2Fe alloy. This model is more particularly adapted to transition metals, and gives realistic densities of states.

PACS. 61.44.-n Semi-periodic solids – 61.66.Dk Alloys – 71.10.-w Theories and models of many electron systems

1 Introduction

This work is part of a more general study of local order in quasicrystals or complex structures. We want to study stability *versus* local atomic displacement, in these alloys, so we first need to find a description of the electronic structure, which remains valid up to the second order of any (atomic) perturbation.

We have chosen charge transfer as the order parameter. It is indeed partly responsible for the electronic distribution in transition metals, and was already pointed out as a potentially rich parameter [1]. In addition, we were interested in making an analytical work on these electronic states, so that we could apply it in further studies on the atomic structure: the choice of charge transfer proved indeed very efficient in that line. More precisely, we have used Slater screening corrections to calculate the charge transfers, which on top allows a nice description of the atomic structure. Then, we have built a new model, which may be decomposed as follow.

– In a first step, we give an explicit analytical expression of the effective Hamiltonian: We began from Friedel's determination of the *d*-band in transition metals [2], since the first steps of his calculation apply to nonperiodic order. He ignored some overlapping interatomic terms, which limits its validity to first order; however, one could since long remedy this shortcoming, by using Non-orthogonal Tight-Binding approximation (NTB), where overlapping interatomic terms are included [3]. So we developed a new NTB formalism, in which charge transfer is the local order parameter. In all literature, only numerical calculations have been done so far, so this is the first explicit analytical calculation of energetical terms with a realistic geometrical environment, in the case of complex alloys.

– Then, we use the moment method, introduced by Haydock, but we refined the recurence equations, in order to include exactly all overlapping terms.

– Eventually, we get an analytical equation for the charge transfer.

This model is also presented elsewhere [4]. We only consider electrons in the $3d$ (valence) band. The atomic lattice is fixed, and each atomic element is characterized by its core charge Z_i (nucleus charge plus core electrons). The charge transfer simply writes $\delta N = N_i - Z_i$, where N_i is the real charge level ($N_c = 2 - h$ conduction electrons, where h is a uniform hibridization coefficient, and $N_v = N_i - 2 + h$ valence electrons); we chose $h = 1$. Here, $3d$ electrons are free from intraatomic interactions.

We have calculated numerically the charge transfers for Ti_2Fe f.c.c. alloy. There are 96 atoms per unit cell, and this crystal, which has symetry O_h^7, is an approximant of a quasicrystal. We obtain very realistic values (about 0.5 electrons), contrarily to all previous simulations using standard Tight-Binding approximation, which overestimate the charge transfers [5].

The density of states we have calculated, has a similar shape than those obtained from Linear Muffin-Tin Orbital (LMTO) calculations [6], although some peaks are moved. This is by itself very satisfactory, and indicates that our model is consistent, since we use no adjustable parameter (instead of [5], for instance). Thus, we can be more confident with the charge values we calculate.

I will now present the detailed analytic calculation of a charge transfer, which suports the new NTB model, then the numerical computation of the charge transfers in a Ti_2Fe crystal, by a self-similar recurrence method. We will afterwards discuss our numerical results.

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$$\begin{aligned}
&\sum_{k_1\, m_1\, m_2} |k_1 32 m_1\rangle \Bigl(\langle k_1 32 m_1 | \frac{p^2}{2\mu} + V_{k_1} | k_1 32 m_2 \rangle + \sum_{k_o \neq k_1} \langle k_1 32 m_1 | V_{k_o} | k_1 32 m_2 \rangle \Bigr) a_{k_1 m_2} \\
&- \sum_{\substack{k_1 <> k_2 \\ m_1\, m_2\, m_3}} |k_1 32 m_1\rangle \langle k_1 32 m_1 | k_2 32 m_2 \rangle \Bigl(\langle k_2 32 m_2 | \frac{p^2}{2\mu} + V_{k_2} | k_2 32 m_3 \rangle \\
&+ \sum_{k_o \neq k_2} \langle k_2 32 m_2 | V_{k_o} | k_2 32 m_3 \rangle \Bigr) a_{k_2 m_3} + \sum_{\substack{k_1 <> k_2 \\ m_1\, m_2}} |k_1 32 m_1\rangle \Bigl(\langle k_1 32 m_1 | \frac{\mathbf{p}^2}{2\mu} + V_{k_1} + V_{k_2} | k_2 32 m_2 \rangle \\
&+ \sum_{\substack{k_o \neq k_1 \\ \neq k_2}} \langle k_1 32 m_1 | V_{k_o} | k_2 32 m_2 \rangle \Bigr) a_{k_2 m_2} + \cdots = E \sum_{k_1\, m_1} a_{k_1 m_1} | k_1 32 m_1 \rangle
\end{aligned}$$

2 Analytic calculation of the charge transfer

We expand an electronic state $|\phi\rangle$ in the orbital basis $\{|knlm\rangle\}$, where atom k (in position R_k) is the center, and $|nlm\rangle$ is the usual hydrogenate state; $|knlm\rangle$ obeys equation:

$$\left(\frac{p^2}{2\mu} - \frac{Z_k^* q^2}{4\pi\epsilon_o |\mathbf{r} - \mathbf{R}_k|} \right) |knlm\rangle = \frac{E_k}{n^2} |knlm\rangle \qquad (1)$$

where standard quantum mechanics gives $E_k = -Z_k^{*2} E_I$, $E_I = q^2 \big/ 8\pi\epsilon_o a_o \simeq 13.6$ eV, $a_o \simeq 0.53$ Å is Bohr radius, and $Z_k^* = Z_k - (N_k - 3 + h)\eta_s$ is the screened core charge seen by the electron at site k with $\eta_s = 0.35$ [7]. Here again, we will only consider $n = 3$ and $l = 2$.

Then $|\phi\rangle = \sum a_{km} |k32m\rangle$ obeys Schrödinger's equation:

$$\Bigl(\frac{p^2}{2\mu} + \sum_k V_k \Bigr) |\phi\rangle = \frac{E_k}{9} |\phi\rangle \qquad (2)$$

where $V_k = (N_k - Z_k) q^2 \big/ 4\pi\epsilon_o |\mathbf{r} - \mathbf{R}_k|$ if the electron is at site $i \neq k$, and V_k is defined in (1) otherwise.

We will now expand (2) on the same basis. We must insist on the fact that $\{|knlm\rangle\}$ is not orthogonal, and therefore, the usual closure relation does not hold. Instead, we will use the generalised closure relation (*cf.* Appendix A):

$$\begin{aligned}
Id = &\sum_{j=1}^{\infty} (-1)^{j+1} \\
&\times \sum_{\substack{k_1 \neq k_2 \neq \cdots \neq k_j \\ m_1 \cdots m_j}} |k_j 32 m_j\rangle \langle k_j 32 m_j | \cdots | k_1 32 m_1 \rangle \langle k_1 32 m_1 | \qquad (3)
\end{aligned}$$

then, multiplying, on the left we get

See equations above.

We write $V_k |k32m\rangle = (E_k/9 - p^2/2\mu) |k32m\rangle$ from (1), and

$$\langle k_1 32 m_1 | V_{k_o} | k_2 32 m_2 \rangle \sim \langle k_1 32 m_1 | k_2 32 m_2 \rangle V_{k_o} \Bigl(\frac{R_{k_1} + R_{k_2}}{2} \Bigr)$$

then comes:

$$\begin{aligned}
&\sum_{k_1\, m_1\, m_2} |k_1 32 m_1\rangle \bigl(E_{k_1} \delta_{m_1\, m_2} + \sum_{k_o \neq k_1} I^{k_o}_{\substack{k_1 \\ m_1\, m_2}} \bigr) a_{k_1 m_2} \\
&+ \sum_{\substack{k_1 <> k_2 \\ m_1\, m_2}} |k_1 32 m_1\rangle \Bigl\{ S_{\substack{k_1 \ k_2 \\ m_1\, m_2}} \Bigl(E_{k_1} - I^{k_1}_{\substack{k_2 \\ m_1\, m_2}} \\
&+ \sum_{\substack{k_o \neq k_1 \\ \neq k_2}} \Bigl(V_{k_o} \bigl(\frac{R_{k_1} + R_{k_2}}{2} \bigr) - V_{k_o} (R_{k_2}) \bigr) \Bigr) \Bigr) - T_{\substack{k_1 \ k_2 \\ m_1\, m_2}} \Bigr\} a_{k_2 m_2} \\
&+ \cdots = E \sum_{k_1\, m_1} a_{k_1 m_1} |k_1 32 m_1\rangle
\end{aligned}$$

where the shift integral $I^{k_o}_{\substack{k_1 \\ m_1\, m_2}} = \langle k_1 32 m_1 | V_{k_o} | k_1 32 m_2 \rangle$, and the overlapping interatomic integrals $S_{\substack{k_1 \ k_2 \\ m_1\, m_2}} = \langle k_1 32 m_1 | k_2 32 m_2 \rangle$ and $T_{\substack{k_1 \ k_2 \\ m_1\, m_2}} = \langle k_1 32 m_1 | \frac{p^2}{2\mu} | k_2 32 m_2 \rangle$ we need to calculate explicitely.

2.1 Shift integral

The shift integral writes:

$$I^{k_o}_{\substack{k_1 \\ m_1\, m_2}} = \int dr\, r^2 d\Omega \; |f_{32}(r)|^2 \frac{(N_{k_1} - Z_{k_1}) q^2}{4\pi\epsilon_o |\mathbf{r} - \mathbf{R}_o|} \bar{Y}_2^{m_1}(\Omega) Y_2^{m_2}(\Omega) \qquad (4)$$

where

$$\begin{aligned}
\mathbf{R}_o &\equiv \mathbf{R}_{k_o} - \mathbf{R}_{k_1}, \\
f_{32}(r) &= -\sqrt{2/5} (\lambda_{k_1})^{7/2} (2/3) r^2 e^{-r\lambda_{k_1}}
\end{aligned}$$

is the radial wave function (we put $\lambda_k = Z_k^*/(3a_o)$) and Y_l^m is the normalized spherical harmonics. Then we use the standard angular expansion:

$$\begin{aligned}
\frac{1}{|\mathbf{r} - \mathbf{R}_o|} = &\sum_{k=0}^{\infty} \sum_{m=-k}^{k} \frac{4\pi}{2k+1} \frac{\inf(r, R_o)^k}{\sup(r, R_o)^{k+1}} \\
&\times (-1)^m Y_k^m(\Omega) Y_k^{-m}(\Omega_o)
\end{aligned}$$

which gives:

$$\begin{aligned}I^{k_1}_{\substack{k_o\\ m_1\,m_2}} &= \frac{8}{45}\frac{(N_{k_1}-Z_{k_1})q^2}{4\pi\epsilon_o}(2\lambda_{k_1})^7\\ &\times\sum_{k=0}^{\infty}\sum_{m=-k}^{k} Y_k^{-m}(\Omega_o)\int dr\, r^6 e^{-2\lambda_{k_1}r}\frac{\inf(r,R_o)^k}{\sup(r,R_o)^{k+1}}\\ &\times\int d\Omega\,\bar{Y}_2^{m_1}(\Omega)Y_2^{m_2}(\Omega)\frac{4\pi}{2k+1}Y_k^m(\Omega).\end{aligned}$$

The second integral writes $\sqrt{4\pi/(2k+1)}\langle k\,2\,(m_1-m_2)\,m_2|2\,m_1\rangle\times\langle k\,2\,0\,0|2\,0\rangle$ and is not zero when $k=0,2,4$ and $m=m_1-m_2$ [8]. Including factor $Y_k^{-m}(\Omega_o)$, we obtain corresponding angular representation $K^{(k)}(\Omega_o)$, which are given in Appendix B. For the first integral we use [9] and finally get:

$$\begin{aligned}I^{k_1}_{\substack{k_o\\ m_1\,m_2}} &= \frac{a_o}{R_o}\delta_{m_1\,m_2}\\ &\times\Big(1-e^{-2u}\big(1+\frac{5}{3}u+\frac{4}{3}u^2+\frac{2}{3}u^3+\frac{2}{9}u^4+\frac{2}{45}u^5\big)\Big)\\ &+\frac{126}{(Z^*_{k_1})^2}\big(\frac{a_o}{R_o}\big)^3K^{(2)}_{m_1\,m_2}(\Omega_o)\Big(1-e^{-2u}\big(+2u+2u^2\\ &+4u^3+\frac{2}{3}u^4+\frac{11}{42}u^5+\frac{5}{63}u^6+\frac{u^7}{63}\big)\Big)\\ &+\frac{25515}{(Z^*_{k_1})^4}\big(\frac{a_o}{R_o}\big)^5K^{(4)}_{m_1\,m_2}(\Omega_o)\\ &\times\Big(1-e^{-2u}\big(1+2u+2u^2+\frac{4}{3}u^3+\frac{2}{3}u^4+\frac{4}{15}u^5\\ &+\frac{4}{45}u^6+\frac{8}{315}u^7+\frac{2}{315}u^8+\frac{2}{63}u^9\big)\Big)\end{aligned}\tag{5}$$

where $u=\lambda_{k_1}R_o$ and the exponential terms may be neglected, as shown from further numerical computations.

2.2 Two-center integral

The interatomic two-center term writes:

$$\begin{aligned}S_{\substack{k_1\;k_2\\ m_1\,m_2}} &= \int \mathbf{dr}_1\,\mathbf{dr}_2\;\bar{f}_{32}(r_1)f_{32}(r_2)\bar{Y}_2^{m_1}(\Omega_1)Y_2^{m_2}(\Omega_2)\\ &\times\boldsymbol{\delta}(\mathbf{r}_1-\mathbf{r}_2-\mathbf{R}_{12})\end{aligned}\tag{6}$$

$$\begin{aligned}&=\frac{8}{45}(\lambda_{k_1}\lambda_{k_2})^{7/2}\int\mathbf{dr}_1\,\mathbf{dr}_2\;r_1^2e^{-\lambda_{k_1}r_1}r_2^2e^{-\lambda_{k_2}r_2}\\ &\times\bar{Y}_2^{m_1}(\Omega_1)Y_2^{m_2}(\Omega_2)\boldsymbol{\delta}(\mathbf{r}_1-\mathbf{r}_2-\mathbf{R}_{12})\end{aligned}$$

where $\mathbf{R}_{12}\equiv\mathbf{R}_{k_1}-\mathbf{R}_{k_2}$. Then, we rotate all coordinates $\mathbf{u}\to\mathcal{R}(R_{12})\mathbf{u}$, following notations in [10], and find a similar expression, with now a factor

$$\sum_{m'_1=-2}^{2}\sum_{m'_2=-2}^{2}D^{(2)}_{m'_1\,m_1}\big(\mathcal{R}^{-1}(\mathbf{R}_{12})\big)D^{(2)}_{m'_2\,m_2}\big(\mathcal{R}^{-1}(\mathbf{R}_{12})\big)\tag{7}$$

and m_1, m_2 become m'_1, m'_2 in the integral.

Integration over azimutal coordinates ϕ_1, ϕ_2 just brings $2\pi\delta_{m'_1\,m'_2}$; $\pm m_1$ give equal contributions. Using:

$$\begin{aligned}\cos(\theta_1) &= \big(r_1^2+R_{12}^2-r_2^2\big)\Big/(2r_1R_{12})\\ \cos(\theta_2) &= \big(r_1\cos(\theta_1)-R_{12}\big)\Big/r_2\\ \sin(\theta_2) &= r_1\sin(\theta_1)\Big/r_2\end{aligned}$$

which induces:

$$\begin{aligned}Y_2^{\pm2}(\Omega_2) &= \left(\frac{r_1}{r_2}\right)^2Y_2^{\pm2}(\Omega_1)\\ Y_2^{\pm1}(\Omega_2) &= \left(\frac{r_1}{r_2}\right)^2Y_2^{\pm1}(\Omega_1)-\frac{\sqrt{5}r_1R_{12}}{r_2^2}Y_1^{\pm1}(\Omega_1)\\ Y_2^{0}(\Omega_2) &= \left(\frac{r_1}{r_2}\right)^2Y_2^{0}(\Omega_1)-\frac{\sqrt{15}r_1R_{12}}{r_2^2}Y_1^{\pm1}(\Omega_1)\\ &+\frac{\sqrt{5}}{2r_2^2}(3R_{12}^2+r_1^2-r_2^2)Y_0^0\end{aligned}$$

and including the complex phase factor, (7) becomes:

$$\begin{aligned}&\sum_{|m'_1|=0}^{2}D^{(2)}_{m'_1\,m_1}\big(\mathcal{R}^{-1}(\mathbf{R}_{12})\big)D^{(2)}_{m'_1\,m_2}\big(\mathcal{R}^{-1}(\mathbf{R}_{12})\big)e^{i\phi_{12}(m_2-m_1)}\\ &\qquad=\sum_{m=0}^{2}L^{(2m)}(\Omega_{12})\end{aligned}$$

with $L^{(0)}=Id$, $L^{(2)}=(7K^{(2)}-Id)/3$ and $L^{(4)}=12K^{(4)}/5+4K^{(2)}/3-4Id/105$, which happen to write just like orthogonal projectors (see Appendix B).

Now the remaining integral only depends on $m=|m'_1|=0,1,2$. Using [9] and MATHEMATICA language, we finally get:

$$\begin{aligned}S_{\substack{k_1\;k_2\\ m_1\,m_2}} &= \sum_{m=0}^{2}L^{(2m)}\left(\frac{2\sqrt{u_1u_2}}{u_1^2-u_2^2}\right)^7\big(e^{-iu_2}P_m(u_1,u_2)\\ &-e^{-iu_1}P_m(u_2,u_1)\big)\end{aligned}\tag{8}$$

where $u_i=\lambda_{k_i}R_{12}$ and P_m are rational polynomials, given in Appendix C.

When $u_1\to u_2$, (8) is indeterminate, and is replaced by

$$S_{\substack{k_1\;k_2\\ m_1\,m_2}}=\sum_{m=0}^{2}L^{(2m)}e^{-iu_1}P_m^{lim}(u_1)\tag{8bis}$$

where P_m^{lim} are rational polynomials, given in Appendix C.

For T, we write:

$$\frac{p^2}{2\mu}|k_132m_1\rangle=-\frac{\hbar^2}{2\mu}\frac{\partial}{r^2\partial r}\left(r^2\frac{\partial .}{\partial r}\right)+\frac{L^2}{2\mu r^2}|k_132m_1\rangle$$

and the corresponding radial wave function is:

$$\begin{aligned}&-\frac{\hbar^2}{2\mu}\frac{\partial}{r^2\partial r}\left(r^2\frac{\partial f_{32}}{\partial r}\right)+\frac{6\hbar^2f_{32}}{2\mu r^2}\\ &\qquad=-\frac{2}{3}\sqrt{\frac{2}{5}}(\lambda_{k_1})^{\frac{7}{2}}(6\lambda_{k_1}r-\lambda_{k_1}^2r^2)e^{-\lambda_{k_1}}\end{aligned}$$

$$
\begin{aligned}
&a_{k_1m_1}\Big(-\frac{{Z^*_{k_1}}^2}{18}+\sum_{k_o\neq k_1}\frac{(N_{k_o}-Z_{k_o})a_o}{|R_{k_o}-R_{k_1}|}\Big)+\sum_{m_2}a_{k_1m_2}\Big(\sum_{k_o\neq k_1}(N_{k_o}-Z_{k_o})\Big[\frac{126a_o^3K^{(2)}}{|R_{k_o}-R_{k_1}|^3{Z^*_{k_1}}^2}+\frac{25515a_o^5K^{(4)}}{|R_{k_o}-R_{k_1}|^5{Z^*_{k_1}}^4}\Big]\Big)\\
&+\sum_{\substack{k_1<>k_2\\ m_2}}a_{k_2m_2}\sum_{m=0}^{2}L^{(2m)}\Big[\Big(-\frac{{Z^*_{k_1}}^2}{18}+\frac{(N_{k_1}-Z_{k_1})a_o}{|R_{k_2}-R_{k_1}|}+\varDelta_3\Big)g_m(\lambda_{k_1}(R_{k_2}-R_{k_1}),\lambda_{k_2}(R_{k_2}-R_{k_1}))\\
&-\frac{Z^*_{k_1}Z^*_{k_2}}{18}h_m(\lambda_{k_1}(R_{k_2}-R_{k_1}),\lambda_{k_2}(R_{k_2}-R_{k_1}))\Big]=\tilde{E}a_{k_1m_1} \qquad (9)
\end{aligned}
$$

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and, substituing in (6) f_{32} by the latter, we get similar expressions to (8) or (8bis), with new polynomials Q_m and $Q_m^{\lim}$ (given in Appendix C).

2.3 Effective Hamiltonian

Putting all expressions together, and doing all approximations that come straightforward, we finally get:

See equation (9) above

where $g_m(x,y)=\left(\frac{2\sqrt{x,y}}{x^2-y^2}\right)^7\left(e^{-iy}P_m(x,y)-e^{-ix}P_m(y,x)\right)$ when $x\neq y$ and $g_m(x,y)=e^{-ix}P_m^{lim}(x,x)$ otherwise; and the same for h_m with Q_m or Q_m^{lim}. $\tilde{E}$ is expressed in Rydberg; and

$$\varDelta_3=\sum_{\substack{k_o\neq k_1\\ \neq k_2}}(N_{k_o}-Z_{k_o})\left(\frac{a_o}{|\frac{R_{k_1}+R_{k_2}}{2}-R_{k_o}|}-\frac{a_o}{|R_{k_2}-R_{k_o}|}\right)$$

may be neglected, as shown from further numerical computations.

This is exactly the formula after (6) in reference [4], therefore we have explicitely calculated the effective Hamiltonian $\tilde{H}$, in terms of local parameters R_k and band levels N_k. In place of N_k, we can also use charge transfer N_k-Z_k, which will be chosen as the local order parameter.

2.4 Charge transfer equation

With these explicit expression of S and $\tilde{H}$, we can now develop the energy moments a_i, b_i, through the recurrence equation given in [4]. Then, using the formulas given in [11], we can express the $3d$ band level N_v in terms of these moments. Since $N_k=N_v+N_c$ where we took N_c constant $\simeq 1$, we have eventually expressed the charge transfer N_k-Z_k in terms of itself and local parameters.

The computation of the solution of this equation, the fact it exists and is unique, remain then a matter of numerical analysis, which we have performed successfully.

3 Numerical calculation of the charge transfers of Ti_2Fe

We wanted an alloy made of transition metals, so we chose Ti_2Fe alloy, in which a stable quasicrystalline phase has been discovered [12]. But we chose an approximant f.c.c. phase, where there are only three non equivalent sites, to make this first numerical computation easier. There are 96 atoms in the unit cell; in fact, all the 32 iron atoms are located at the vertices of tetrahedra (Wyckoff position e); while 64 titanium atoms form complex structures around those tetrahedra: 48 equivalent titanium (Wyckoff position f) have the same distance from the iron atoms, we will call them Tia; while the left 16 equivalent titanium (Wyckoff position c) are more distant. If you consider the polygon formed by the 22 first-near neighbourgs of a tetrahedron, 12 Tia atoms have five neighbourgs, 6 Tia atoms have six neighbourgs (they seem inequivalent because we only consider one tetrahedron), and the 4 left Tib atoms also have six neighbourgs. In the whole bulk, Fe and Tib atoms have 12 first-neighbours, while Tia has 14 [13].

As explained in [4], we need no Slater-Koster parameters now, since the Hamiltonian $\tilde{H}$ is explicitely known, with all non-diagonal and non-orthogonal exact terms. If you except h, the only free variable is the charge transfer, which we calculate self-consistently.

Moreover, we impose a strict electronic neutrality during all the calculations (we are only considering a bulk), which keeps the shift integral not too high. This brings equation $2N_{\mathrm{Fe}}+3N_{\mathrm{Ti}a}+N_{\mathrm{Ti}b}=2Z_{\mathrm{Fe}}+3Z_{\mathrm{Ti}a}+Z_{\mathrm{Ti}b}$ where the ($3d$)-band levels correspond to the three non-equivalent sites. This numerical calculation gives no troubles, except for the factor containing exponentials and polynomilas, like in (8), which raises gorgeous numerical precision difficulties. To solve them, we have used several Taylor-Young developments, the order of which are depending on $|\lambda_{k_1}-\lambda_{k_2}|$, which we got through MATHEMATICA language. We carefully verified that our solution is unique and that all our terms had significant influence in the results, we also examined the influence of all possible errors: for instance, we could not determinate exactly the band limits in our energetic spectrum; we also found that the exponential factor, in the shift integral, is neglectible, which is not surprising but very satisfactory since this factor is of the same order as the second-neighbour corrections, which we skipped at first.

Following all these prescriptions, we obtained very realistic densities of electronic state curves (Fig. 1), which are similar to those obtained from LMTO calculations [6], and therefore are very satisfactory. More precisely, the comparison of the partial densities of Fe shows a good fit, while it is average for Tia and even bad for Tib (our main peack is moved on the left). So, only comparing with

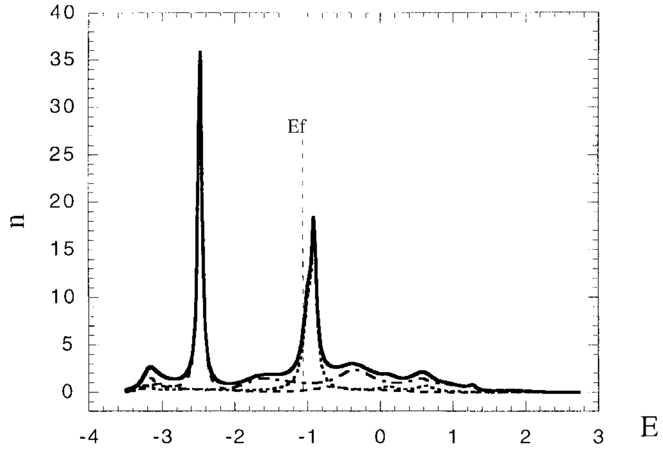

Fig. 1. Total density of electronic states (solid line) of Ti_2Fe in a f.c.c. approximant phase, and corresponding partial densities of states of Fe (dashed line), Tia (dot-dashed line) and Tib (dotted line).

experimental data could discriminate between these theoretical predictions. On top, it is impossible to extract any charge transfer value from the LMTO computation, whereas we obtain $\delta N_{\mathrm{Fe}} = 0.417$, $\delta N_{\mathrm{Ti}a} = -0.063$ and $\delta N_{\mathrm{Ti}b} = -0.103$.

The signs of the charge transfers are not surprising. Iron atoms, which are more electronegative than titanium, will form negative clusters, while the Tia and Tib atoms around will charge positively.

Finally, we have investigated the influence of the hybridization parameter h which proves small.

4 Conclusion

By this method one could successfully predict the electronic structure of valence electrons, in terms of charge transfers. It seems particularly well adapted to complex structures, for which we give the electronic density of states after not very long computer calculations. We point again here that the structure has been then characterized in detail for all atoms, and takes into account their real local environment.

It is straightforward to extend our formulas to the case of second or third series transition metals. Since we take very roughly into account all hybridization mechanism, it is not so obvious to apply the model to small elements like Aluminium, although one might thing that charge transfer takes this hybridization into account, in an approximate way.

Therefore, we intend to apply our method to complex structures, such as the α phase of Mn, the β phase of W, or the i phase of NiCr [14] *etc.* But the major development will be the study of electronic modifications when an atom is moved, in the purpose of investigating the stability of local defects in those complex structures, in particular in quasicrystals.

I would like to thank Françoise Dénoyer, Marie-Catherine Desjonquères, Daniel Spanjaard and Guy Trambly for fruitful discussions or advices.

Appendix A

Let us consider $N = S - Id$; when the interatomic overlapping terms are not too big, the $\mathcal{L}_\infty$ norm $\|N\| < 1$, thus S is reversible and

$$Id = S^{-1}S = S\big(Id - N + N^2 - N^3 + \cdots\big)$$

and (3) follows readily.

Appendix B

It is easier to calculate the angular matrix in the real basis formed upon $(|xy\rangle, |yz\rangle, |zx\rangle, |x^2-y^2\rangle, |3z^2-r^2\rangle)$. We then calculate the following expressions: $K^{(0)} = Id$, $K^{(2)} = PMP^\dagger$ and $K^{(4)} = PNP^\dagger$, where

$$P = \big(\mathbf{v}_1\, \mathbf{v}_2\, \mathbf{v}_3\, \mathbf{v}_4\, \mathbf{v}_5\big)\,,$$

$$M = \frac{1}{7}\begin{pmatrix} -2 & 0 & 0 & 0 & 0 \\ 0 & -2 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 2 \end{pmatrix},$$

$$N = \frac{1}{21}\begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & -4 & 0 & 0 \\ 0 & 0 & 0 & -4 & 0 \\ 0 & 0 & 0 & 0 & 6 \end{pmatrix}.$$

$$\text{Here } \mathbf{v}_1 = \begin{pmatrix} \cos(\theta)\cos(2\phi) \\ -\sin(\theta)\cos(\phi) \\ \sin(\theta)\sin(\phi) \\ -\cos(\theta)\sin(2\phi) \\ 0 \end{pmatrix},$$

$$\mathbf{v}_2 = \begin{pmatrix} \frac{1}{4}(\cos(2\theta)+3)\sin(2\phi) \\ -\frac{1}{2}\sin(2\theta)\sin(\phi) \\ -\frac{1}{2}\sin(2\theta)\cos(\phi) \\ \frac{1}{4}(\cos(2\theta)+3)\cos(2\phi) \\ \frac{\sqrt{3}}{4}(1-\cos(2\theta)) \end{pmatrix},$$

$$\mathbf{v}_3 = \begin{pmatrix} -\sin(\theta)\cos(2\phi) \\ -\cos(\theta)\cos(\phi) \\ \cos(\theta)\sin(\phi) \\ \sin(\theta)\sin(2\phi) \\ 0 \end{pmatrix},$$

$$\mathbf{v}_4 = \begin{pmatrix} \frac{1}{2}\sin(2\theta)\sin(2\phi) \\ \cos(2\theta)\sin(\phi) \\ \cos(2\theta)\cos(\phi) \\ \frac{1}{2}\sin(2\theta)\cos(2\phi) \\ -\frac{\sqrt{3}}{2}\sin(2\theta) \end{pmatrix},$$

$$\mathbf{v}_5 = \begin{pmatrix} \frac{\sqrt{3}}{4}(\cos(2\theta)-1)\sin(2\phi) \\ -\frac{\sqrt{3}}{2}\sin(2\theta)\sin(\phi) \\ -\frac{\sqrt{3}}{2}\sin(2\theta)\cos(\phi) \\ \frac{\sqrt{3}}{4}(\cos(2\theta)-1)\cos(2\phi) \\ -\frac{3}{4}\cos(2\theta)-\frac{1}{4} \end{pmatrix}$$

are orthonormal.

and $L^{(0)}$ is the orthogonal projector on $\mathbf{v}_5$, $L^{(2)}$ on $(\mathbf{v}_3, \mathbf{v}_4)$ and $L^{(4)}$ on $(\mathbf{v}_1, \mathbf{v}_2)$.

Appendix C

Through MATHEMATICA, we calculate:

$$\begin{aligned}P_0(u,v) = u\Big(16\Big[30\big(-36(v+v^2)+u^2v-17v^3+u^2v^2-5v^4\big)-u^4v+12u^2v^3-31v^5\Big]\\ +u^6+5u^4v^2+67u^2v^4-73v^6-u^6v-5u^4v^3+13u^2v^5-7v^7+\frac{u^6v^2}{3}-u^4v^4+u^2v^6-\frac{v^8}{3}\Big)\end{aligned}$$

$$\begin{aligned}P_1(u,v) = u\Big(240\Big[2\big(24(v+v^2)-u^2v+11v^3-u^2v^2+3v^4\big)-u^2v^3+v^5\Big]\\ +u^6+21u^4v^2-45u^2v^4+23v^6-u^6v+3u^4v^3-3u^2v^5+v^7\Big)\end{aligned}$$

$$\begin{aligned}P_2(u,v) = u\Big(24\Big[10\big(-12(v+v^2)+u^2v-5v^3+u^2v^2-v^4\big)-u^4v+2u^2v^3-v^5\Big]\\ +u^6-3u^4v^2+3u^2v^4-v^6\Big)\end{aligned}$$

$$\begin{aligned}Q_0(u,v) = 96\Big[90(u^2+v^2+u^2v+v^3)-2u^4+39u^2v^2+43v^4-2u^4v+9u^2v^3+13v^5\Big]\\ +4u^6-60u^4v^2+108u^2v^4+268v^6-3u^6v-31u^4v^3-9u^2v^5+43v^7\\ +3u^6v^2-u^4v^4-7u^2v^6+5v^8-\frac{u^6v^3}{3}+u^4v^5-u^2v^7+\frac{v^9}{3}\end{aligned}$$

$$\begin{aligned}Q_1(u,v) = 48\Big[4\big(-30(u^2+v^2+u^2v+v^3)+u^4-12u^2v^2-14v^4+u^4v-2u^2v^3-4v^5\big)\\ +2u^4v^2+u^2v^4-3v^6\Big]-7u^6v-3u^4v^3+27u^2v^5-17v^7+u^6v^2-3u^4v^4+3u^2v^6-v^8\end{aligned}$$

$$\begin{aligned}Q_2(u,v) = 48\Big[30(u^2+v^2+u^2v+v^3)-2u^4+9u^2v^2+13v^4-2u^4v-u^2v^3+3v^5\Big]\\ +6u^6+6u^4v^2-30u^2v^4+18v^6-u^6v+3u^4v^3-3u^2v^5+v^7\end{aligned}$$

and the limit of $\Big(e^{-u}P_m(v,u)-e^{-v}P_m(u,v)\Big)(uv)^{7/2}\Big/\Big((u^2-v^2)^7e^{-u}\Big)$, when $v\mapsto u$, is:

$$P_0^{lim}(u) = 1+u+\frac{5u^2}{21}-\frac{2u^3}{21}-\frac{2u^4}{35}-\frac{u^5}{315}+\frac{u^6}{315}$$

$$P_1^{lim}(u) = 1+u+\frac{2u^2}{7}-\frac{u^3}{21}-\frac{u^4}{21}-\frac{u^5}{105}$$

$$P_2^{lim}(u) = 1+u+\frac{3u^2}{21}+\frac{2u^3}{21}+\frac{u^4}{105}$$

$$Q_0^{lim}(u) = 1+u+\frac{u^2}{35}-\frac{32u^3}{105}-\frac{8u^4}{105}+\frac{u^5}{21}-\frac{u^6}{315}$$

$$Q_1^{lim}(u) = 1+u+\frac{4u^2}{35}-\frac{23u^3}{105}-\frac{3u^4}{35}+\frac{u^5}{105}$$

$$Q_2^{lim}(u) = 1+u+\frac{13u^2}{35}+\frac{4u^3}{105}-\frac{u^4}{105}.$$

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