Indirect Mn-Mn pair interaction induces pseudogap in Al(Si)-Mn approximants

Guy Trambly de Laissardi`ere\textsuperscript{a} \textsuperscript{1}, Duc Nguyen-Manh\textsuperscript{b}, Didier Mayou\textsuperscript{c}

\textit{a) Laboratoire de Physique Théorique et Modélisation, CNRS-Université de Cergy-Pontoise (UMR 8089), Neuville, 95031 Cergy-Pontoise, France.}
\textit{b) Department of Materials, University of Oxford, Oxford, Parks Road, OX1 3PH, United Kindom.}
\textit{c) Laboratoire d’Etudes des Propriétés Electronique des Solides (CNRS), 38042 Grenoble Cédex 9, France.}

2002/9/6

The effect on the electronic structure of an indirect Mn-Mn interaction mediated by the valence states and the sp-d hybridisation is presented. In Al(rich)-Mn phases related to quasicrystals (Al\textsubscript{12}Mn, \textgreek{o}-Al\textsubscript{6}Mn, \textgreek{a}-Al\textsubscript{9}Mn\textsubscript{2}Si), this indirect interaction creates a Hume-Rothery pseudogap in the density of states together with a minimisation of the band energy. It is shown that the Mn-Mn interaction up to the distance around 10-20 Å plays an essential role in stabilizing related quasicrystal structures.

\textit{Keywords:} Quasicrystal; Approximant; Hume-Rothery stabilization; Pseudogap; Transition-metal.

1. Introduction

Al(rich)-Mn and Al(rich)-Si-Mn systems, contain many crystalline approximants of quasicrystals. These phases are good examples to analyse the effect of the position of transition metal (TM) atoms in stabilizing complex structure related to quasiperiodicity. The origin of the stabilization of quasicrystals is still unclear in spite of many experimental and theoretical study. For Al-based quasicrystals, a Hume-Rothery mechanism \textsuperscript{4} \textsuperscript{4} \textsuperscript{4} \textsuperscript{4} have been shown to play a significant role (see for instance \textsuperscript{3} \textsuperscript{3} \textsuperscript{3} \textsuperscript{3} and Refs. within). In these phases, the average number of electron per atom (ratio \textit{e}/\textit{a}) is an important parameter. Indeed, the occurrence of phases related to quasicrystals is explained by the fact that they are electron compounds with similar \textit{e}/\textit{a} ratio in spite of different constituents and different atomic concentrations \textsuperscript{1} \textsuperscript{1} \textsuperscript{1} \textsuperscript{1}. A band energy minimisation occurs when the Fermi sphere touches a pseudo-Brillouin zone, constructed by Bragg vectors \textit{K}_p corresponding to intense peaks in the experimental diffraction pattern. The Hume-Rothery condition for alloying is then \textit{2k}_F \simeq \textit{K}_p. Assuming a free electron valence band, the Fermi momentum, \textit{k}_F, is calculated from \textit{e}/\textit{a}.

In sp Hume-Rothery alloys, valence electrons (sp electrons) are nearly free. Their density of states (DOS) is well described by the Jones theory \textsuperscript{4} \textsuperscript{4} \textsuperscript{4} \textsuperscript{4} \textsuperscript{4}. The Fermi-sphere / pseudo-Brillouin zone interaction creates a depletion in the DOS, called pseudogap, near the Fermi energy \textit{E}_F. Such a pseudogap has been found experimentally and from first-principles calculations in many sp quasicrystals and approximants \textsuperscript{4} \textsuperscript{4} \textsuperscript{4} \textsuperscript{4} \textsuperscript{4}. It has also been...
found in many icosahedral approximants containing TM elements \cite{14,15} whereas there are contradictory results about decagonal phases (Ref. \cite{12} and Refs. within). But, the treatment of Al(rich)-TM is more complicated as d states of TM are not nearly-free states. In the case of crystals and icosahedral quasicrystals it has been shown \cite{13,14} that sp-d hybridisation increases a pseudogap. In some particular cases a pseudogap may also be induced by the sp-d hybridisation \cite{13,14}. The Hume-Rothery stabilization can also be viewed as a consequence of oscillating pair interactions between atoms (Refs. \cite{3,19} and Refs. in there). In this direction Zou and Carlsson have shown that an indirect Mn-Mn interaction, mediated by sp states of Al, is strong enough to favours Mn-Mn distances close to 4.7 Å in Al(rich)-Mn quasicrystals and approximants. Here, it is shown that an indirect Mn-Mn interaction up to 10-20 Å induces pseudogap at $E_F$ in the approximants: cubic Al$_2$Mn \cite{14} orthorhombic o-Al$_5$Mn \cite{14}, and cubic o-Al$_5$Mn$_2$Si \cite{20}. The importance of Mn-Mn interaction up to large distances shows the complexity of the stabilizing process. Obviously “frustration” mechanism should occur that may favour for complex atomic structures. As Al$_2$Mn, o-Al$_5$Mn and o-Al$_5$Mn$_2$Si are related to quasicrystals, this study suggests that a Hume-Rothery stabilization, expressed in terms of Mn-Mn interaction, is intrinsically linked to the emergence of quasiperiodic structures in Al(Si)-Mn systems.

2. Effective Bragg potential for Al(rich)-Mn alloys

For sp Hume-Rothery alloys, the valence states (sp states) are nearly-free states scattered by a weak potential (Bragg potential, $V_B$). In this section, we show briefly that in sp-d Hume-Rothery alloys, sp electrons feel an “effective Bragg potential” \cite{14,12} that takes into account the strong effect TM atoms via the sp-d hybridisation.

Following a classical approximation \cite{16,17} for Al(Si)-Mn alloys, a simplified model is considered where sp states are nearly-free and d states are localized on Mn sites $i$. The effective hamiltonian for the sp states is written:

$$H_{eff}(sp) = \frac{\hbar^2 k^2}{2m} + V_{B,eff}$$  \hspace{1cm} (1)

where $V_{B,eff}$ is an effective Bragg potential that takes into account the scattering of sp states by the strong potential of Mn atoms. $V_{B,eff}$ depends thus on the positions $r_i$ of Mn atoms. Assuming that all Mn atoms are equivalent and that two Mn atoms are not first-neighbour, one obtains \cite{14,12}:

$$V_{B,eff}(r) = \sum_{\mathbf{K}} V_{B,eff}(\mathbf{K}) e^{i\mathbf{K} r_i}, \hspace{1cm} (2)$$

$$V_{B,eff}(\mathbf{K}) = V_B(\mathbf{K}) + \frac{|f_{\mathbf{K}}|^2}{E - E_d} \sum_i e^{-i\mathbf{K} r_i}, \hspace{1cm} (3)$$

where the vectors $\mathbf{K}$ belong to the reciprocal lattice, $f_{\mathbf{K}}$ is a average matrix element that couples sp states $\mathbf{k}$ and $\mathbf{k} - \mathbf{K}$ via the sp-d hybridisation, and $E_d$ is the energy of d states. The term $V_B(\mathbf{K})$ is a weak potential independent with the energy $E$. It corresponds to the Bragg potential for sp Hume-Rothery compounds.

The last term in equation (3), is due to the d resonance of the wave function by the potential of Mn atoms. It is strong in an energy range $E_d - \Gamma \leq E \leq E_d + \Gamma$, where $2\Gamma$ is the width of the d resonance. This term is essential as it does represent the diffraction of the sp electrons by a network of d orbitals, i.e. the factor ($\sum_i e^{-i\mathbf{K} r_i}$) corresponding to the structure factor of the TM atoms sub-lattice. As the d band of Mn is almost half filled, $E_F \simeq E_d$, this factor is important for energy close to $E_F$. Note that the Bragg planes associated with the second term of equation (3) correspond to Bragg planes determined by diffraction.

This analysis shows that both sp-d hybridisation and diffraction of sp states by the sub-lattice of Mn atoms are essential to understand the electronic structure of Al(Si)-Mn alloys \cite{12}. The strong effect of sp-d hybridisation on the pseudogap is then understood in the framework of Hume-Rothery mechanism.
3. Two Mn in the Al(Si) matrix

As a Hume-Rothery stabilization is a consequence of oscillation of the charge density of the valence electrons with energy close to $E_F$, a most stable atomic structure is obtained when distances between atoms are multiples of the wavelength of electrons with energy close to $E_F$. Since the scattering of valence sp states by the Mn sub-lattice is strong, the Friedel oscillations of charge of sp electrons around Mn must have a strong effect on a stabilization. Therefore a Hume-Rothery mechanism in Al(rich)-Mn compounds might be analysed in term of a Mn-Mn pair interaction resulting from a strong sp-d hybridisation. Zou and Carlson [21, 22] have calculated this interaction from an Anderson model hamiltonian with two impurities, using a Green’s function method. It is found that a specific Mn-Mn distance of 4.7 Å favours for a stabilization of Al-Mn approximants [21]. As 4.7 Å is larger than first neighbour distances, this shows the existence of an indirect medium range Mn-Mn interaction. The indirect interaction is mediated by sp-d hybridisation where sp states are mainly Al states.

We calculated the indirect Mn-Mn pair interaction $\Phi_{Mn-Mn}$ from the transfer matrix $T$ of two Mn atoms in the free electrons matrix by using the Lloyd formula [23] (Fig. 1). According to classical approximation for metal, a phenomenological short range repulsive term should be add. But this term is not important in the present study as we analyse only the medium range order, i.e. distances larger than first-neighbour distances (see Fig. 1). Parameters of the calculation are: the Fermi energy $E_F$ fixed by the Al matrix ($E_F = 11.7$ eV), the width of the d resonance $2\Gamma$ which increases as the sp-d hybridisation increases ($2\Gamma = 2.7$ eV), and the energy $E_d$ of the d resonance which depends on the nature of the transition metal atom ($E_d = 11.37$ eV corresponding to ~5.8 d electrons per Mn atom). A small variation of these parameters does not modify qualitatively the results presented in the following. In this paper only non-magnetic Mn are considered as most of Mn are non-magnetic in quasicrystals and approximants [24,25,26]. In particular Al$_{12}$Mn, o-Al$_6$Mn and o-Al$_9$Mn$_2$Si are non magnetic [24]. Because of the sharp Fermi surface of Al, $\Phi_{TM-TM}$ oscillated (Friedel oscillations of the charge density). It asymptotic form at large TM-TM distance ($r$) is of the form:

$$\Phi_{TM-TM}(r) \propto \frac{\cos(2k_F r - \delta)}{r^3}. \quad (4)$$

The phase shift $\delta$ depends on the nature of the TM atom and varies from $2\pi$ to 0 as the d band fills. Magnitude of the medium range interaction is larger for Mn-Mn than for other transition metal (Cr, Fe, Co, Ni, Cu), because the number of d electrons close to $E_F$ is the largest for Mn, and the most delocalized electrons are electrons with Fermi energy. The effect analysed here is then more important for Al-rich alloys containing Mn element than for alloys containing other TM elements.

The total DOS of two Mn atoms in the free electrons matrix is:

$$n(E, r) = n^0_{sp}(E) + \Delta n_{2Mn}(E, r), \quad (5)$$

where $n^0_{sp}$ is the free electron DOS and $\Delta n_{2Mn}$, the variation of the total DOS due to two Mn atoms. $\Delta n_{2Mn}$ depends on the Mn-Mn distance $r$. When $r$ is very large (almost infinity), each Mn are similar to Mn impurity thus: $\Delta n_{2Mn} =$
2\Delta n_{1Mn}$, where $\Delta n_{1Mn}$ is the well known Lorentzian of the virtual-bound states. But small deviation from the Lorentzian occurs for finite $r$. On Fig. 2, $\Delta n_{2Mn}(E)$ is drawn for different values of $r$. $r = 3.8$ Å and $r = 5.8$ Å correspond to positive Mn-Mn interaction, whereas $r = 4.8$ Å and $r = 6.7$ Å correspond to minima of the interaction (see arrows on Fig. 1).

4. Effect of Mn sub-lattice on electronic structure of approximants

4.1. Density of states

In this section, the effect of indirect Mn-Mn interaction on the DOS of approximants is analysed. We focus on the case of cubic Al$_{12}$Mn, orthorhombic $\alpha$-Al$_6$Mn and cubic $\alpha$-Al$_9$Mn$_2$Si. These calculations include effects of all Mn-Mn pairs up to Mn-Mn distance equal to $R$ (R in Å). V.B.S. is the Lorentzian of one Mn impurity in the free electron matrix (virtual-bound state).
Mn atoms are not first-neighbour. In metallic alloys, the main aspects of the DOS are consequences of short range and medium range atomic order. The effect of the medium range order on the pseudogap at Fermi energy is estimated from a simple model that takes only into account the Mn-Mn pair effects with Mn-Mn distances larger than first-neighbour distances. An important question is to determine the distance up to which an indirect Mn-Mn interaction is essential.

Assuming a Hume-Rothery mechanism for the stabilization, the electronic energy is a sum of pair interaction. As interaction magnitudes are larger for Mn-Mn than for Al-Mn and Al-Al [27], the pseudo gap at Fermi energy is estimated from a simple model that takes only into account Mn-Mn interaction is essential. The electronic energy is a sum of Mn-Mn interaction up to Mn-Mn distance larger than 25% [28], are neglected. In this model, the total DOS, \( n_R(E) \), is calculated as the sum of the variation of the DOS due to each Mn-Mn pair:

\[
\Delta n_R(E) = n_{sp}^0(E) + \Delta n_R(E),
\]

\[
\Delta n_R(E) = x \Delta n_{1Mn}(E)
\]

\[
+ \sum_{r_{ij}<R} \left( \Delta n_{2Mn}(E, r_{ij}) - 2 \Delta n_{1Mn}(E) \right),
\]

where \( i, j \) are index of Mn atom, \( r_{ij} \) is Mn-Mn distance, and \( x \), the number of Mn atoms. \( \Delta n_{2Mn} \) is defined by equation (6). \( \Delta n_{1Mn} \) is the variation of the DOS due to one Mn impurity in the free electron matrix: virtual-bound state (V.B.S.). \( \Delta n_{1Mn} \) is a Lorentzian centered at energy \( E_d \) with a width at half maximum equal to 2Γ. \( n_{sp}^0 \) is the total DOS computed by taking into account all Mn-Mn interaction up to Mn-Mn distance equal to \( R \). \( \Delta n_R \) is the part of \( n_R \) due to Mn atoms.

\( \Delta n_R(E) \) of Al\(_{12}\)Mn, o-Al\(_6\)Mn and α-Al\(_6\)Mn\(_2\)Si are shown in Fig.3 for different values of distance \( R \). First Mn-Mn distance is 6.47 Å in Al\(_{12}\)Mn, 4.47 Å in o-Al\(_6\)Mn and 4.61 Å in α-Al\(_6\)Mn\(_2\)Si, but a well pronounced pseudogap appeared only when the Mn-Mn interactions up to 10-20 Å are taken into account.

Negative value of \( \Delta n_R(E) \) induces reduction of the total DOS with respect to the free electron value \( n_{sp}^0 \). For o-Al\(_6\)Mn, the minimum of the pseudogap corresponds to \( \Delta n_R \approx 0 \). The total DOS at the minimum of the pseudogap is thus similar to pure Al DOS, in agreement with first-principles calculation [14]. But for Al\(_{12}\)Mn and α-Al\(_6\)Mn\(_2\)Si, as \( \Delta n_R < 0 \), a reduction of the total DOS with respect to free electron case is due to Mn-Mn medium range interaction. First-principles studies [4, 10] have already shown a reduction. The present work enlightens a particular effect of Mn atoms in these ab initio results.

4.2. Energy

The “structural energy”, \( \mathcal{E} \), of the Mn sub-lattice in Al host is defined as the energy needed to built the Mn sub-lattice in the metallic host that simulates Al (and Si) host from isolated Mn atoms in the same metallic host. \( \mathcal{E} \) per unit cell is:

\[
\mathcal{E} = \sum_{i,j \neq i}^{1} \frac{1}{2} \Phi_{Mn-Mn}(r_{ij}) e^{-\frac{r_{ij}}{L}},
\]

\( L \) depends on the structural quality and temperature and can be estimated to be larger than 10 Å. \( \mathcal{E}(L) \) for Al\(_{12}\)Mn, o-Al\(_6\)Mn and α-Al\(_6\)Mn\(_2\)Si are shown on Fig.4. \( \mathcal{E} \) are always negative with magnitude strong enough to give a significant contribution to the band energy. This result is in good agreement with effect of Mn-Mn interactions on the pseudogap as shown previously. According to a Hume-Rothery mechanism, one expects that a pseudogap is well pronounced for a large value of \( |\mathcal{E}| \).

5. Conclusion

A simple model is presented that allows to enlighten effects of Mn atoms on the electronic structure in Al(rich)-Mn phases related to quasicrystals. It is shown that an indirect Mn-Mn interaction up to distances 10-20 Å is essential in stabilizing, as it creates a Hume-Rothery pseudogap close to \( E_F \). The band energy is then minimised.
Fig. 4: Structural energy $\mathcal{E}(L)$ of Mn sub-lattice versus the mean-free path $L$ (in Å).

The effect of an indirect Mn-Mn interactions has been also study in previous works \cite{21, 22, 27, 12, 29}. Recently \cite{12}, it explained the origin of a large vacancies in the hexagonal $\beta$-$\text{Al}_9\text{Mn}_3\text{Si}$ and $\varphi$-$\text{Al}_{10}\text{Mn}_3$ phases, whereas similar site are occupied by Mn in $\mu$-$\text{Al}_{12}\text{Mn}$ and $\lambda$-$\text{Al}_4\text{Mn}$, and by Co in $\mu$-$\text{Al}_4\text{Co}_2$. On the other hand, medium range indirect Mn-Mn interaction is also determinant for the existence or not of magnetic moments in Al-Mn quasicrystals and approximants \cite{29}.

As Al(rich)-Mn phase structure are related to those of quasicrystals, it suggests that a Hume-Rothery stabilization, governs by this Mn-Mn interaction, is intrinsically linked to the emergence of quasiperiodicity.

References

[1] T.B. Massalski, U. Mizutani, Prog. Mater. Sci. 22 (1978) 151.
[2] A.T. Paxton, M. Methfessel, D.G. Pettifor, Proc. R. Soc. Lond. A 453 (1997) 1493.
[3] D. Mayou, in Lecture on Quasicrystals ed. F. Hippert and D. Gratias (Les Ulis, Les Editions de Physique, 1994) p 417.
[4] E. Belin-Ferré, in this conference.
[5] U. Mizutani, T. Takeuchi, H. Sato, in this conference.
[6] A.P. Tsai, A. Inoue, T. Masumoto, Sci. Rep. Ritu. A 36 (1991) 99.