Conditions on the Occurrence of Magnetic Moments in Quasicrystals and Related Phases

Guy Trambly de Laissardièrea, Didier Mayoub

a) Laboratoire de Physique Théorique et Modélisation, Université de Cergy-Pontoise, Neuville, 95031 Cergy-Pontoise, France; and Laboratoire Léon Brillouin, CEA-CNRS Saclay, France.
b) Laboratoire d’Etudes des Propriétés Electronique des Solides (CNRS), 38042 Grenoble Cédex 9, France.

1999/10/12

Abstract

We analyze the criterion for the appearance of magnetic moments in quasicrystals approximants and liquids Al-Mn. In a Hartree-Fock scheme, it is shown that the Stoner criterion \( (U_n d_\uparrow d_\downarrow) \geq 1 \) does not apply to these systems due to the presence of the pseudogap in the density of states. We give an generalized criterion that can take into account the particular density of state. The main result is that the appearance of a magnetic moment on a Mn atom depends strongly on its position in the crystalline structure. Indeed some particular positions of the Mn atoms lead to magnetic moments whereas other positions are more stable when the Mn is non-magnetic. This criterion is used to analyzed the electronic structure of two approximants (1/1-Al-Pd-Mn-Si and T-Al-Pd-Mn) calculated by the self-consistent LMTO-ASA method.

Keywords: Magnetism; Localized Moment; Quasicrystal; Approximant.

1. Introduction

The magnetic properties of quasicrystals have been studied since the discovery of icosahedral Al-Mn phase. The main focus of this article is the existence of local moments carried by Mn atoms. In crystals (Al\(_6\)Mn, Al\(_{12}\)Mn...) and some approximants (\(\alpha\) - and \(\beta\)-Al-Mn-Si...) the Mn atoms do not carry a magnetic moment ("non-magnetic" atoms, spin \(gS = m = 0\)). In icosahedral Al-Mn, Al-Pd-Mn and many of their approximants (\(\mu\)-Al\(_4\)Mn, 1/1-Al-Pd-Mn-Si, T-Al-Pd-Mn...) most of the Mn atoms are non-magnetic but few Mn atoms carry a magnetic moment ("magnetic" atoms, \(m \neq 0\)). By contrast, in the liquid in equilibrium with these phases, there is a large proportion of magnetic Mn atoms. See Refs. [1, 2] and Refs. in them.

In Al-Mn alloys, Mn atoms are closed to the magnetic / non-magnetic transition. The magnetic state of Mn depends on the local density of states (local DOS) on Mn atoms [3, 4]. These local DOS is influenced by the local environment and we show that it depends also on the environment up to 5 – 10 \(\text{Å}\). The usual criterion to study the magnetic states of transition metal (TM) atom in non-magnetic host is the Friedel-Anderson criterion (equivalent to the Stoner criterion for a TM impurity in a non-metallic host). This criterion assumes that sp valence states are free states, but in crystals and quasicrystals that is no more valid and it is necessary to generalize the criterion.

2. Generalized Stoner criterion

The magnetic state of a TM atom in aluminum host results from the competition between the Coulomb interaction and the kinetic energy of the d electrons. The Coulomb interaction is \( \mathcal{E}_C = U N_{d\uparrow} N_{d\downarrow} = \frac{U}{2} (N_{d\uparrow} - m^2) \), where \( N_d \) (\( N_d = N_{d\uparrow} + N_{d\downarrow} \)) is the total number of d electrons and \( m = N_{d\uparrow} - N_{d\downarrow} \) is the local magnetic moment on the TM atom. \( \mathcal{E}_C \) decreases when \( m \) increases, so it favors the occurrence of a magnetic moment (\( m \neq 0 \)). The kinetic en-
energy (or band energy), $\Delta$, of the d electrons increases when the hybridization between the d orbital and the sp nearly free states increases. Roughly speaking $\Delta$ is proportional to width of the local d DOS. Therefore, the understanding of magnetic moment requires to analyze carefully the local DOS. In the Al-Mn alloys, because of the strong sp-d hybridization, the local DOS depends widely on the atomic structure: the local environment (number and chemical nature of the neighbors, local symmetry) must be important, but it depends also on the medium range order because the sp states are delocalized. This last effect is the most important for Mn atoms as respect with other TM atoms (Cr, Fe, Co, Ni), because the d band of Mn is half filled. In the following we analyze this effect.

Let us recall first the case of one Mn impurity in a non-metallic Al host described by the well known Virtual Bound States model for which one d orbital is coupled with the sp free states. The result of this model is independent of the position of the Mn atom in the alloy. The Mn d DOS is a Lorentzian that satisfies the rigid band model, i.e. the d DOS is shifted when the on site energy, $E_d$, varies but its shape does not change. In the Hartree approximation, the energy $E_d$ is obtained by the self consistent relation:

$$E_d,\sigma = E_d^0 + U(N_{d,-\sigma} - N_{d,-\sigma}^0) . \tag{1}$$

$N_{d,\sigma}$ and $N_{d,\sigma}^0$ are the number of d electrons for a Mn atom with spin $\sigma$ in the alloys, and for an isolated Mn atom, respectively. From the rigid band model, the criterion of the appearance of a localized moment is easy to calculate by writing these self consistent equations for the spin up and the spin down. It follows that a localized moment exists if (local Stoner criterion):

$$U_{\text{nd}}(E_F) \geq 1 , \tag{2}$$

For Mn atoms in a metallic host we have to consider 5 degenerated d orbitals per Mn impurity. The exchange integral $J$ between two electrons, localized on two different orbitals of the same Mn impurity, is taken into account by changing U to (U−4J).

As shown experimentally and theoretically the DOS of the quasicrystals and their approximants is characterized by the presence of a well defined pseudogap in the vicinity of the Fermi energy ($E_F$) which contributes to their stabilization (Hume-Rothery mechanism). The band energy is minimized when the number of valence electrons is such that the Fermi sphere touches a "predominant Brillouin zone", constructed by the Bragg planes located in the vicinity of the Fermi sphere. The diffraction by Bragg planes splits the valence sp states into bonding and antibonding states. That leads to the formation of a valley, called pseudogap, in the partial sp DOS near $E_F$. The energies of bonding (antibonding) states are mainly below (above) the pseudogap. Because of the diffraction by Bragg planes, there is no more translation invariance of valence state amplitudes. Therefore the hybridization between the nearly free sp states and a d orbital depends strongly on the Mn position, $r_d$, of the Mn atom in the alloys. In particular, it has been shown that the partial d DOS on Mn exhibits a pseudogap or not, depending on the Mn position. Schematically, one find that there are two extreme cases depending on $r_d$ via the parameter $\alpha(r_d)$, $\alpha(r_d) = (\cos(K.r_d + \Phi))$. Here, $K$ are the wave vectors of the reciprocal lattice that define the Bragg plane from which the pseudo-Brillouin zone is constructed, and $\Phi$ is a phase depending on the lattice. If $\langle \cos(K.r_d + \Phi) \rangle = 1$, the amplitude of the bonding valence states is maximized at $r = r_d$, and the amplitude of the antibonding valence states is maximized at $r = r_d$. Thus the d orbital is more coupled with the bonding valence states. On the other hand, if $\langle \cos(K.r_d + \Phi) \rangle = -1$, the d orbital is more coupled with the bonding valence states.

Moreover due to the large diffraction by Bragg plane, the rigid band model hypothesis for the local d DOS is no more valid. The Friedel-Anderson criterion for the appearance of a localized moment (equation (2)) has to be generalized. The revised criterion, calculated from the equations (1), is:

$$-U \frac{\partial N_d}{\partial E_d} \geq 1 , \tag{3}$$

where $N_d$ is the number of d electrons of Mn in the non-magnetic case.

One defines the energy $U_{\text{lim}}$ as the interaction energy above which the Mn atom is magnetic (Fig. 1). The first difference with the Virtual Bound State is that $U_{\text{lim}}$ varies with the position $r_d$ via the parameter $\langle \cos(K.r_d + \Phi) \rangle$.

The calculated $U_{\text{lim}}$ gives also a satisfying model to understand the difference between the magnetism of Al-Mn crystals, quasicrystals and liquids. Whereas most of Mn atoms are non-magnetic in crystals and quasicrystals, it has been found from ab initio calculations and experimental measurements that the liquid Al-Mn exhibit a large amount of localized magnetic moments. In the crystals, d orbitals of stable Mn atoms are preferentially coupled with antibonding sp states, $\langle \cos(K.r_d + \Phi) \rangle \approx 1$ (see Refs. 1, 3 and next section); $U_{\text{lim}}$ is given by the curve Fig. 1, which takes into account the diffraction by Bragg planes. But in liquid, the topological disorder destroys the diffraction by Bragg plane and $U_{\text{lim}}$ is given by the curve Fig. 1. As the temperature increases through the fusion, the $U_{\text{lim}}$ decreases, and the Mn should go from a non-magnetic state to a magnetic state.
3. Energetic criterion

The generalized criterion presented in the last section can be analyzed in terms of band energy. We calculated the energy of Mn atoms in low concentration in Al host (Fig. 2), assuming a important diffraction by Bragg plane. This model is described elsewhere. To understand by simple arguments as follows. If the Mn atom is non-magnetic its energy varies with its position, $r_d$, but the energy of the Mn atoms with a high moment does not vary with $r_d$. Indeed the magnetic Mn atoms are less influenced by their environment because their d bands are not close to $E_F$ when in fact the most delocalized electron are electrons with energy $E_F$. In the studied alloys the hybridization between the atoms is important and the electronic energy of the Mn atoms is minimized for the Mn positions $r_d$ satisfying $\langle \cos(K \cdot r_d + \Phi) \rangle \simeq 1$. In that case, the Mn is non magnetic and the d DOS calculation exhibits a pseudogap near $E_F$. By contrast the Mn atomic positions $\langle \cos(K \cdot r_d + \Phi) \rangle \simeq -0.3$, that are less stable, lead to magnetic Mn and no pseudogap near $E_F$ in the d DOS.

Provided that the Mn concentration is not too small, the pseudo-potential on the atomic sites which scatters the valence electron is mainly due to the Mn atoms themselves (the Al pseudo-potential being much weaker), and the pseudogap results mainly from the diffraction of the valence states by the sublattice of the Mn atoms. This effect can be analyzed in term of a long range effective pair potential (up to $\sim 10 \text{ Å}$) which moreover depends on the magnetic state of Mn. Therefore the magnetic state depends also on the medium range order of the Mn atoms.

4. LMTO calculations for approximant

The electronic structure and the magnetic structure of 1/1-approximant and a Taylor phase are performed by using the self-consistent linear muffin tin orbital method (LMTO-ASA). We studied the $1/1 - \text{Al}_{5.9}\text{Pd}_{12.1}\text{Mn}_{14.6}\text{Si}_{7.3}$ containing 123 atoms in a cubic cell. The lattice parameter is $a = 12.281 \text{ Å}$. Two Wyckoff sites (noted Mn(4) and Mn(5)) are occupied by Mn atoms. The total DOS and the local DOS on Al, Mn(4) and Mn(5), calculated without spin-polarization, are shown on Fig. 3. The local DOS on Al, that correspond mainly with valence sp states, exhibits a pseudogap near $E_F$ as expected for an approximant. The local DOS on the two Mn sites differs markedly. Mn(4) DOS is split into bonding and anti-bounding states separated by the pseudogap. In contrast, there is no pseudogap at $E_F$ on Mn(5) DOS.

The spin polarized LMTO calculation converges to a non-magnetic state ($m = 0$) on Mn(4) and on Pd; but there is a localized magnetic moment on Mn(5), $m = gS \simeq 0.7$. Mn(4) is surrounded by 10 Al atoms, which favors a strong sp-d hybridization and therefore a non-magnetic states. On the other hand, Mn(5) atom is surrounded by 5 Mn(5) and 7 Al. The d-d overlapping between Mn(5) atoms is strong and the sp-d hybridization is less important that for Mn(4). It follows that Mn(5) in a good candidate to be magnetic.

The composition domain of the Taylor phase is rather wide. Five Wyckoff sites (noted Mn(1) to Mn(5)) are occupied by Mn only and five Wyckoff sites (noted TM(1) to TM(5)) by Al/Mn mixture with different Al/Mn ratios. We calculated the electronic structure for a Mn-low T-phase and we assumed that TM(1) to TM(5) are occupied by Al atoms only and that TM(6) is occupied by Pd atoms only. There are 156 atoms in a orthorhombic unit.

Fig. 1. Criterion for the appearance of a localized magnetic moment on Mn in Al host (see text). $\alpha = \langle \cos(K \cdot r_d + \Phi) \rangle$. With diffraction by Bragg plane: (a) Stoner criterion, $U^{\lim} = 1/n_d(E_F)$. (b) generalized criterion, $U^{\lim} = -1/(\partial N_d/\partial E_d)$. (c) without diffraction by Bragg planes (Virtual Bound State hypothesis), $U^{\lim} = -1/(\partial N_d/\partial E_d) = 1/n_d(E_F)$.

Fig. 2. Variation $\Delta \varepsilon$ (eV) of the energy due to one Mn d impurity in a metallic host as function of $\alpha = \langle \cos(K \cdot r_d + \Phi) \rangle$. Full line, with diffraction by Bragg planes. Dashed line, without diffraction by Bragg planes (impurity case).
Fig. 3. Electronic structure of the 1/1-Al_{65.9}Pd_{12.2}Mn_{14.6}Si_{7.3}, calculated by LMTO-ASA without spin polarization: total DOS; sum of local DOS on Al sites; local DOS on Mn(4); and local DOS on Mn(5). $E_F = 0$.

Fig. 4. Total DOS of T-Al_{79.5}Pd_{5.1}Mn_{15.4}, calculated by LMTO-ASA. $E_F = 0$.

5. Conclusion

In Al-Mn-(Si) and Al-Pd-Mn-(Si) quasicrystals and their approximants many Mn atoms are close to the magnetic / non-magnetic transition. We show that the magnetic state is determined by the local DOS on Mn atoms which depends on their local environment and also on their environment up to $5 - 10$ Å. The Mn atoms located on the less stable atomic position could be magnetic, while the Mn atoms located in the most stable position are non-magnetic.

References

[1] V. Simonet et al., in these Conference.
[2] F. Hippert et al., Phys. Rev. Lett. 76 (1996) 54.
[3] G. Trambly de Laissardiére, D. Mayou, D. Nguyen Manh, Europhys. Lett. 21 (1993) 25; G. Trambly de Laissardiére et al., J. Non-Cryst. Solids 153-154 (1993) 430.
[4] J. Hafner, M. Krajčí, Phys. Rev. B 57 (1998) 2849; M. Krajčí, J. Hafner Phys. Rev. B 58 (1998) 14110.
[5] T. Fujiwara, T. Yokokawa, Phys. Rev. Lett. 66 (1991) 333.
[6] E. Belin et al., Europhys. Lett. 26 (1994) 677.
[7] G. Trambly de Laissardiére et al., Phys. Rev. B 52 (1995) 7920.
[8] M. Krajčí, J. Hafner, M. Mihalkovic, Phys. Rev. B 55 (1997) 843.
[9] J. Friedel, Can. J. Phys. 34 (1956) 1190; P.W. Anderson, Phys. Rev. 124 (1961) 41.
[10] J. Friedel, Helv. Phys. Acta. 61 (1988) 538.
[11] A. M. Bratkovsky et al., Phys. Rev. B 52 (1995) 3056.
[12] G. Trambly de Laissardiére, D. Mayou, unpublished.
[13] O. K. Andersen, Phys. Rev. B 12 1975 3060.
[14] K. Sugiyama, N. Kaji, K. Hiraga, Zeitschrift Kristall. 213 (1998) 168.
[15] H. Klein, et al., Phil. Mag. Lett. 75 (1996) 197.