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Effect of transition-metal elements on the electronic properties of quasicrystals and complex aluminides

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1 Introduction

It is with great pleasure that we contribute to this book in honor of Prof. Takeo Fujiwara. GTL enjoyed eighteen months of Prof. Fujiwara's hospitality at the University of Tokyo during the early 1990's. At that time the work of Prof. Fujiwara in the field of electronic structure of quasicrystals had already made a major contribution to the literature (see for instance [1]). Since that time our research owes much to his work.

Prof. Fujiwara was the first who performed realistic calculations of the electronic structure in quasicrystalline materials without adjustable parameters (ab-initio calculations) [2]. Indeed these complex alloys [3] have very exotic physical properties (see Refs. [4, 5] and Refs therein), and it rapidly appeared that realistic calculations on the actual quasicrystalline materials are necessary to understand the physical mechanism that govern this properties. In particular, these calculations allow to analyze numerically the role

of transition-metal elements which is essential in those materials.

In this paper, we briefly present our work on the role of transition-metal element in electronic structure and transport properties of quasicrystals and related complex phases. Several Parts of these works have been done or initiated in collaboration with Prof. T. Fujiwara.

2 Electronic structure

2.1 Ab-initio determination of the density of states

A way to study the electronic structure of quasicrystal is to consider the case of approximants. Approximants are crystallines phases, with very large unit cell, which reproduce the atomic order of quasicrystals locally. Experiments indicate that approximant phases, like α-AlMnSi, α-AlCuFeSi, R-AlCuFe, etc., have transport properties similar to those of quasicrystals [4, 6]. In 1989 and 1991, Prof. Fujiwara performed the first numerical calculations of the electronic structure in realistic approximants of quasicrystals [2, 7, 8]. He showed that their density of states (DOS, see figure 1) is characterized by a depletion near the Fermi energy E_{F}, called *"pseudo-gap"*, in agreement with experimental results (for review see Ref. [4, 9, 18]) and a Hume-Rothery stabilization [10, 11]. The electronic structure of simpler crystals such as orthorhombic Al_6Mn, cubic $Al_{12}Mn$, present also a pseudo-gap near E_{F} which is less pronounced than in complex approximants phases (figure 1) [11].

2.2 Models to analyze the role of transition-metal element

sp–d hybridization model

The role of the transition-metal (TM, TM = Ti, Cr, Mn, Fe, Co, Ni) elements in the pseudo-gap formation has been shown from experiments, ab-initio calculations and model analysis [4,13–19,11]. Indeed the formation of the pseudo-gap results from a strong *sp–d* coupling associated to an ordered

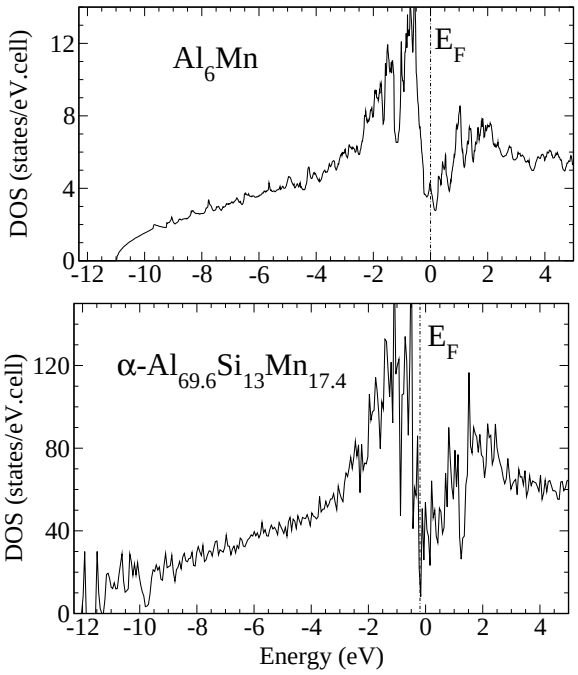

Figure 1: Ab-initio total DOS of Al_6Mn (simple crystal) and α-$Al_{69.6}Si_{13.0}Mn_{17.4}$ (approximant of icosahedral quasicrystals) [11, 12].

sub-lattice of TM atoms [19, 11]. Consequently, the electronic structure, the magnetic properties and the stability, depend strongly on the TM positions, as was shown from ab-initio calculations [28–33,20,21].

How an effective TM–TM interaction induces stability?

Just as for Hume-Rothery phases a description of the band energy can be made in terms of pair interactions (figure 2) [17, 19]. Indeed, it has been shown that an effective medium-range Mn–Mn interaction mediated by the sp(Al)–d(Mn) hybridization plays a determinant role in the occurrence of the pseudo-gap [19]. We have shown that this interaction, up to distances 10–20 Å, is essential in stabilizing these phases, since it can create a Hume-Rothery pseudo-gap close to E_F. The band energy is then minimized as shown on figure 3 [20, 11].

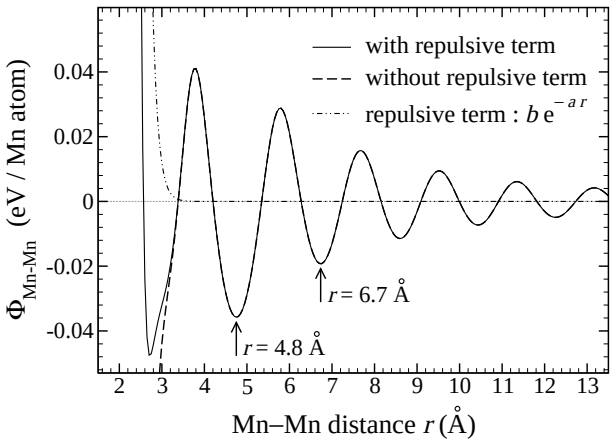

Figure 2: Effective medium-range Mn–Mn interaction between two non-magnetic manganese atoms in a free electron matrix which models aluminum atoms. [11]

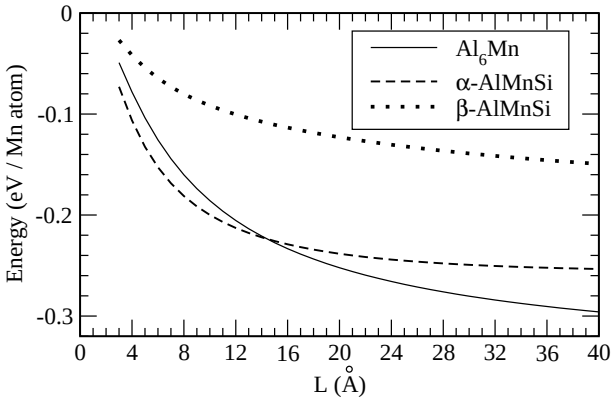

Figure 3: Variation of the band energy due to the effective Mn–Mn interaction in o-Al_6Mn, α-AlMnSi and β-Al_9Mn_3Si. [20]

The effect of these effective Mn–Mn interactions has been also studied by several groups [17, 20, 21] (see also Refs in [11]). It has also explained the origin of large vacancies in the hexagonal β-Al_9Mn_3Si and φ-$Al_{10}Mn_3$ phases on some sites, whereas equivalent sites are occupied by Mn in μ-$Al_{4.12}Mn$ and λ-Al_4Mn, and by Co in Al_5Co_2 [20]. On the other hand, an spin-polarized

effective Mn–Mn interaction is also determinant for the existence (or not) of magnetic moments in AlMn quasicrystals and approximants [21, 22, 32].

The analysis can be applied to any Al(rich)-Mn phases, where a small number of Mn atoms are embedded in the free electron like Al matrix. The studied effects are not specific to quasicrystals and their approximants, but they are more important for those alloys. Such a Hume-Rothery stabilization, governed by the effective medium-range Mn–Mn interaction, might therefore be intrinsically linked to the emergence of quasi-periodicity in Al(rich)-Mn system.

Cluster Virtual Bound states

One of the main results of the ab-initio calculations performed by Prof. Fujiwara for realistic approximant phases, is the small energy dispersion of electrons in the reciprocal space. Consequently, the density of states of approximants is characterized by *"spiky"* peaks [2, 7, 8, 28]. In order to analyze the origin of this spiky structure of the DOS, we developed a model that show a new kind of localization by atomic cluster [23].

As for the local atomic order, one of the characteristics of the quasicrystals and approximants is the occurrence of atomic clusters on a scale of 10–30 Å [25]. The role of clusters has been much debated in particular by C. Janot [24] and G. Trambly de Laissardière [23]. Our model is based on a standard description of inter-metallic alloys. Considering the cluster embedded in a metallic medium, the variation $\Delta n(E)$ of the DOS due to the cluster is calculated. For electrons, which have energy in the vicinity of the Fermi level, transition atoms (such as Mn and Fe) are strong scatters whereas Al atoms are weak scatters. In the figure 4 the variation, $\Delta n(E)$, of the density of states due to different clusters are shown. The Mn icosahedron is the actual Mn icosahedron of the α-AlMnSi approximant. As an example of a larger cluster, we consider one icosahedron of Mn icosahedra.

$\Delta n(E)$ of clusters exhibits strong deviations from the Virtual Bound

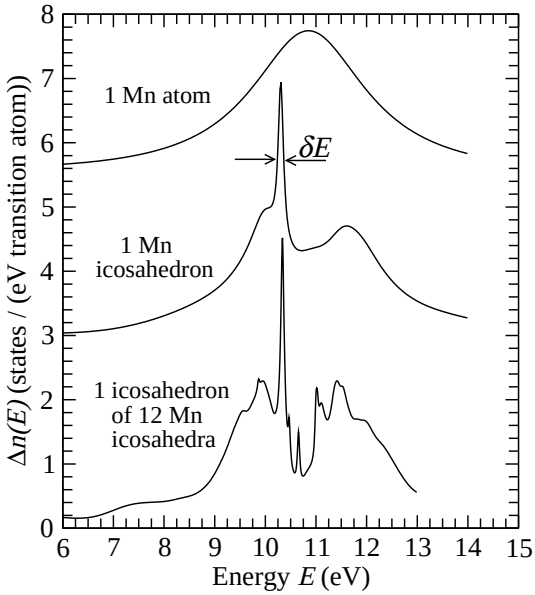

Figure 4: Variation $\Delta n(E)$ of the DOS due to Mn atoms. Mn atoms are embedded in a metallic medium (Al matrix). From [23].

States (1 Mn atom) [26]. Indeed several peaks and shoulders appear. The width of the most narrow peaks ($50 - 100\,\mathrm{meV}$) are comparable to the fine peaks of the calculated DOS in the approximants (figure 1). Each peak indicates a resonance due to the scattering by the cluster. These peaks correspond to states *"localized"* by the icosahedron or the icosahedron of icosahedra. They are not eigenstate, they have finite lifetime of the order of $\hbar/\delta E$, where δE is the width of the peak. Therefore, the stronger the effect of the localization by cluster is, the narrower is the peak. A large lifetime is the proof of a localization, but in the real space these states have a quite large extension on length scale of the cluster.

The physical origin of these states can be understood as follows. Electrons are scattered by the Mn atoms of a cluster. By an effect similar to that of a Faraday cage, electrons can by confined by the cluster provided that their wavelength λ satisfies $\lambda \gtrsim l$, where l is the distance between two Mn spheres. Consequently, we expect to observe such a confinement by the

cluster. This effect is a multiple scattering effect, and it is not due to an overlap between d-orbitals because Mn atoms are not first neighbor.

3 Transport properties

Quasicrystals have many fascinating electronic properties, and in particular quasicrystals with high structural quality, such as the icosahedral AlCuFe and AlPdMn alloys, have unconventional conduction properties when compared with standard inter-metallic alloys. Their conductivities can be as low as 150–200 $(\Omega\,\mathrm{cm})^{-1}$ (see Refs. [4, 5, 27] and Refs. therein). Furthermore the conductivity increases with disorder and with temperature, a behavior just at the opposite of that of standard metal. In a sense the most striking property is the so-called *"inverse Mathiessen rule"* according to which the *increases of conductivity* due to different sources of disorder seems to be *additive*. This is just the opposite that happens with normal metals where the increases of resistivity due to several sources of scattering are *additive*. An important result is also that many approximants of these quasicrystalline phases have similar conduction properties. For example the crystalline α-AlMnSi phase with a unit cell size of about 12 Å and 138 atoms in the unit cell has a conductivity of about 300 $(\Omega\,\mathrm{cm})^{-1}$ at low temperature [4].

3.1 Small Boltzmann velocity

Prof. Fujiwara *et al.* was the first to show that the electronic structure of AlTM approximants and related phases is characterized by two energy scales [2, 7, 8, 28, 29] (see previous section). The largest energy scale, of about $0.5-1\,\mathrm{eV}$, is the width of the pseudogap near the Fermi energy E_{F}. It is related to the Hume–Rothery stabilization via the scattering of electrons by the TM sub-lattice because of a strong sp–d hybridization. The smallest energy scale, less than 0.1 eV, is characteristic of the small dispersion of the band energy $\mathrm{E}(\mathbf{k})$. This energy scale seems more specific to phases related to

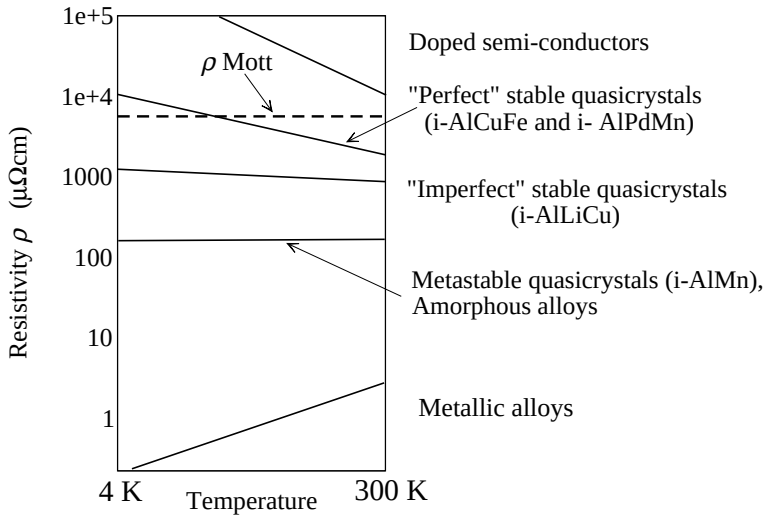

Figure 5: Schematic temperature dependencies of the experimental resistivity of quasicrystals, amorphous and metallic crystals.

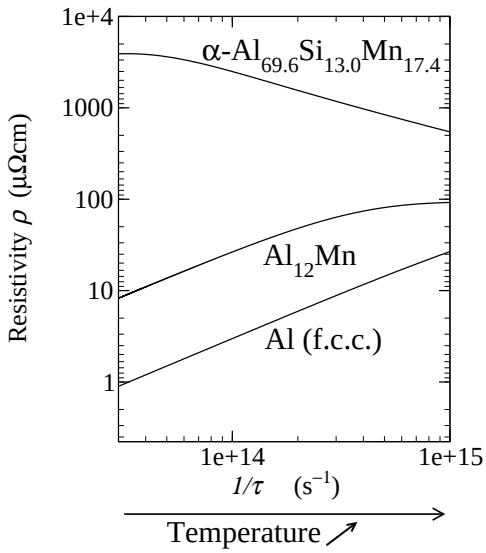

Figure 6: Ab-initio electrical resistivity versus inverse scattering time, in cubic approximant α-$Al_{69.6}Si_{13.0}Mn_{17.4}$, pure Al (f.c.c.), and cubic $Al_{12}Mn$.

the quasi-periodicity. The first consequence on transport is a small velocity at Fermi energy, Boltzmann velocity, $V_{\mathrm{B}} = (\partial E/\partial k)_{E=E_{\mathrm{F}}}$. From numerical calculations, Prof. Fujiwara *et al.* evaluated the Bloch–Boltzmann dc conductivity σ_{B} in the relaxation time approximation. With a realistic value

of scattering time, $\tau \sim 10^{-14}\,\mathrm{s}$ [27], one obtains $\sigma_{\mathrm{B}} \sim 10 - 150\,(\Omega\mathrm{cm})^{-1}$ for a α-AlMn model [8] and 1/1-AlFeCu model [28]. This corresponds to the measured values [4, 6], which are anomalously low for metallic alloys. For decagonal approximant the anisotropy found experimentally in the conductivity is also reproduced correctly [29].

3.2 Quantum transport in Quasicrystals and approximants

The semi-classical Bloch–Boltzmann description of transport gives interesting results for the intra-band conductivity in crystalline approximants, but it is insufficient to take into account many aspects due to the special localization of electrons by the quasi-periodicity (see Refs. [34–43] and Refs. therein). Some specific transport mechanisms like the temperature dependence of the conductivity (inverse Mathiessen rule, the defects influence, the proximity of a metal / insulator transition), require to go beyond a Bloch–Boltzmann analysis. Thus, it appears that in quasicrystals and related complex metallic alloys a new type of breakdown of the semi-classical Bloch-Boltzmann theory operates. In the literature, two different unconventional transport mechanisms have been proposed for these materials. Transport could be dominated, for short relaxation time τ by hopping between "*critical* localized states", whereas for long time τ the regime could be dominated by non-ballistic propagation of wave packets between two scattering events.

We develop a theory of quantum transport that applies to a normal ballistic law but also to these specific diffusion laws. As we show phenomenological models based on this theory describe correctly the experimental transport properties [41, 42, 43] (compare figures 5 and 6).

3.3 Ab-initio calculations of quantum transport

According to the Einstein relation the conductivity σ depends on the diffusivity $D(E)$ of electrons of energy E and the density of states $n(E)$ (summing

the spin up and spin down contribution). We assume that $n(E)$ and $D(E)$ vary weakly on the thermal energy scale kT, which is justified here. In that case, the Einstein formula writes

$$\sigma = e^2 n(E_{\mathrm{F}}) D(E_{\mathrm{F}}) \tag{1}$$

where E_{F} is the chemical potential and e is the electronic charge. The temperature dependence of σ is due to the variation of the diffusivity $D(E_F)$ with temperature. The central quantity is thus the diffusivity which is related to quantum diffusion. Within the relaxation time approximation, the diffusivity is written [41]

$$D(E) = \frac{1}{2} \int_0^{+\infty} C_0(E,t)\, \mathrm{e}^{-|t|/\tau}\, \mathrm{d}t \tag{2}$$

where $C_0(E,t) = \Big\langle V_x(t)V_x(0) + V_x(0)V_x(t) \Big\rangle_E$ it the velocity correlation functions without disorder, and τ is the relaxation time. Here, the effect of defects and temperature (scattering by phonons ...) is taken into account through the relaxation time τ. τ decreases as disorder increases. In the case of crystals phases (such as approximants of quasicrystals), one obtains [42, 43]:

$$\sigma = \sigma_{\mathrm{B}} + \sigma_{\mathrm{NB}} \tag{3}$$

$$\sigma_{\mathrm{B}} = e^2 n(E_{\mathrm{F}})\, V_{\mathrm{B}}^2\, \tau \quad \text{and} \quad \sigma_{\mathrm{NB}} = e^2 n(E_{\mathrm{F}})\, \frac{L^2(\tau)}{\tau} \tag{4}$$

where σ_{B} is actual the Bolzmann contribution to the conductivity and σ_{NB} a non-Boltzmann contribution. $L^2(\tau)$ is smaller than the square of the unit cell size L_0. $L^2(\tau)$ can be calculated numerically for the ab-initio electronic structure [42]. From (3) and (4), it is clear that the Bolzmann term dominates when $L_0 \ll V_{\mathrm{B}}\tau$: The diffusion of electrons is then ballistic, which is the case in normal metallic crystals. But, when $L_0 \simeq V_{\mathrm{B}}\tau$, i.e. when the Bolzmann velocity V_{B} is very low, the non-Bolzmann term is essential. In the case of α-$\mathrm{Al}_{69.6}\mathrm{Si}_{13.0}\mathrm{Mn}_{17.4}$ approximant (figure 7) [42], with realistic value of τ (τ equals a few 10^{-14} s [27]), σ_{NB} dominates and σ increases when

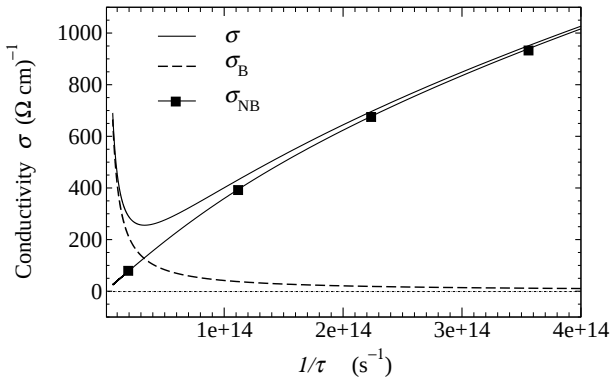

Figure 7: Ab-initio dc-conductivity σ in cubic approximant α-$Al_{69.6}Si_{13.0}Mn_{17.4}$ versus inverse scattering time. [42]

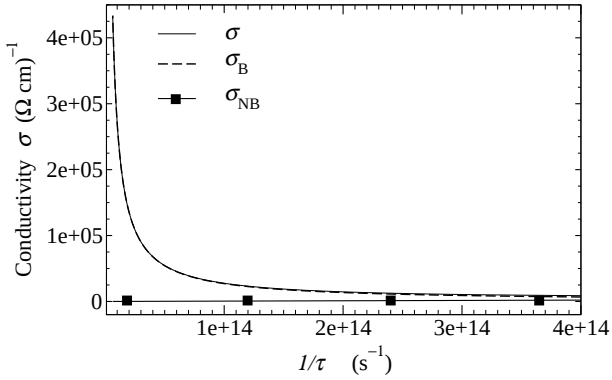

Figure 8: Ab-initio dc-conductivity σ in an hypothetical cubic approximant α-$Al_{69.6}Si_{13.0}Cu_{17.4}$ versus inverse scattering time. [43]

$1/\tau$ increases, i.e. when defects or temperature increases, in agreement with experimental measurement (compare figures 5 and 6).

To evaluate the effect of TM elements on the conductivity, we have considered an hypothetical α-$Al_{69.6}Si_{13.0}Cu_{17.4}$ constructed by putting Cu atoms in place of Mn atoms in the actual α-$Al_{69.6}Si_{13.0}Mn_{17.4}$ structure. Cu atoms have almost the same number of *sp* electrons as Mn atoms, but their *d* DOS is very small at E_F. Therefore in α-$Al_{69.6}Si_{13.0}Cu_{17.4}$, the effect of *sp*(Al)–*d*(TM) hybridization on electronic states with energy near E_F is

very small. As a result, the pseudogap disappears in total DOS, and the conductivity is now ballistic (metallic), $\sigma \simeq \sigma_{\mathrm{B}}$, as shown on figure 8.

4 Conclusion

In this article we present the effect of transition-metal atoms on the physical properties of quasicrystals and related complex phases. These studies lead to consider these aluminides as *spd* electron phases [11], where a specific electronic structure governs stability, magnetism and quantum transport properties. The principal aspects of this new physics are now understood particularly thanks to seminal work of Prof. T. Fujiwara and subsequent developpements of his ideas.

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