Non-collinear magnetism in Al-Mn topologically disordered systems

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Abstract

We have performed the first ab-initio calculations of a possible complex non-collinear magnetic structure in aluminium-rich Al-Mn liquids within the real-space tight-binding LMTO method. In our previous work we predicted the existence of large magnetic moments in Al-Mn liquids [A.M. Bratkovsky, A.V. Smirnov, D. N. Manh, and A. Pasturel, Phys. Rev. B \textbf{52}, 3056 (1995)] which has been very recently confirmed experimentally. Our present calculations show that there is a strong tendency for the moments on Mn to have a non-collinear (random) order retaining their large value of about $3 \mu_B$. The d-electrons on Mn demonstrate a pronounced non-rigid band behaviour which cannot be reproduced within a simple Stoner picture. The origin of the magnetism in these systems is a topological disorder which drives the moments formation and frustrates their directions in the liquid phase.

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The behaviour of magnetic atoms dissolved in simple metals is an active field of research. The magnetic properties of Mn dissolved in an Al matrix are therefore of particular interest since this is a matter of controversy and extensive experimental work, partly aimed at Al-Mn quasicrystals\cite{1,2}. It was long been thought that Mn is unlikely to have a moment in an Al matrix\cite{6} but Cooper and Miljak found that a Mn impurity in fcc Al carries a large moment of $\mu = 3.2 \pm 0.2$ which is apparently screened by $sp$ electrons up to very high temperatures, suggesting a surprisingly high value of the Kondo temperature, $T_K = 600K$\cite{7}.

As for the disordered systems, many authors have reported that at low temperatures ($T < 10K$) only a very small fraction (about 1%) of Mn sites in icosahedral (i-) and amorphous (a-) phases of Al-Mn and Al-Mn-Pd systems is really magnetic and that those atoms have a large moment ($> 1.5 \mu_B$)\cite{2,3}. In the temperature range $T = 10 - 300K$ the value of the magnetic moment on Mn in disordered phases of $Al_{100-x}Mn_x$ alloys varies from $0.7 \mu_B$ (for $x = 16$) to $2.4 \mu_B$ ($x = 45$)\cite{1}, where authors have assumed all Mn atoms to be magnetic. Some data have suggested the existence of a Mn magnetic moment in liquid $Al_{100-x}Mn_x$ of about $\mu_{eff}/\mu_B \sim 2.9, 3.2$ for $x = 20$ and 40\cite{8}, respectively.

Previous theoretical studies have given contradictory results for the magnetic behaviour of Mn in an Al matrix. In Refs.\cite{3,12} the moment on Mn in fcc Al was found to have values varying in the interval 1.74-3.26 $\mu_B$, whereas in calculations\cite{13} and\cite{14} Mn was found to be paramagnetic. Liu et al.\cite{14} found no moment on Mn in MnAl$_n$ clusters with $n < 54$, however, in clusters containing more than one manganese atom the moment appeared.

We have recently performed ab-initio calculations for liquid $Al_{100-x}Mn_x$ ($x=14, 20,$ and 40) to gain more insight into the problem of Mn magnetism in a disordered Al host\cite{15}. Our real-space spin-polarized calculations have shown unambiguously the formation of a large moment of about $3 \mu_B$ on Mn in these metallic liquids. We have demonstrated that the reason for the moment formation lies in a smearing out of the van Hove dip in the density of states which removes the moment in $c$-Al$_6$Mn in accordance with experiment. It means that topological disorder is the origin of the moment formation on Mn in an Al matrix. Our findings have recently been confirmed experimentally by Hippert et al.\cite{5} who
investigated the series of alloys \( \text{Al}_{1-x-y}\text{Pd}_x\text{Mn}_y \) and found that a localized moment appears on Mn atoms in the liquid state and disappears in the solid state. The moment they found is \( 2.76 \pm 0.01 \mu_B \) from susceptibility measurements and \( 2.74 \pm 0.1 \) from the neutron scattering data, in agreement with our calculations [15]. The authors [3] have also observed that, firstly, the moment is \textit{independent} of the Mn concentration thus demonstrating a single atom behaviour. Secondly, the magnetic susceptibility \textit{increases} with temperature. The authors [5] have speculated it could be if only a fraction of the Mn atoms in the liquid bears a localized moment. In this case about 60\% of the Mn atoms can be non-magnetic only if the rest of them carry moments of more than \( 5 \mu_B \), which is unlikely.

In the present study we address the question of the character of magnetic state in Al-Mn liquids, which could have orientational disorder owing to the random sign of the indirect (RKKY) interaction between 3\( d \) ions in a disordered matrix [13]. As has been indicated in Ref. [7] metallic Mn (and Fe as well) is close to a \textit{disordered local moments} regime because it has a half-filled \( d \)-shell and, correspondingly, a large Fermi momentum and a short spatial period of the RKKY oscillations. The antiferromagnetic sign of the Mn-Mn interaction was suggested by Hauser et al. [1] for the case of Al-Mn amorphous alloys and quasicrystals. However, in calculations using the KKR-Green’s function method the Mn-Mn interaction in fcc-Al appeared to be of a \textit{ferromagnetic} sign [1]. It means that only \textit{topological disorder} can produce the random sign of the RKKY interaction on different Mn sites and, therefore, frustrate the otherwise ferromagnetic order.

In the present work we have implemented the method [18] within the \textit{ab initio} real-space tight-binding (RSTB) LMTO formalism, successfully applied before to studies of collinear magnetism in disordered Fe-B and Ni-B [19–21], and Al-Mn systems [15], and we now apply it to self-consistent calculations of the non-collinear magnetic \( \text{Al}_{100-x}\text{Mn}_x \) liquids with \( x=15, 20, \) and 40.

In a system with non-collinear magnetic order the electrons experience an exchange field \( V_{\sigma\sigma'}(\mathbf{r}) \), which depends on the local orientation \( \mathbf{\vec{e}}_R \) \((|\mathbf{\vec{e}}_R|=1)\) of the magnetic moment at each atomic site \( R \) and local electron and spin density.
In constructing the \textit{ab-initio} Hamiltonian, \( H \), we have followed the method by O.K. Andersen \cite{22} and transformed \( H \) into a tight-binding form to make use of the real-space recursion method. The overlap and Hamiltonian matrices in the tight-binding LMTO method were expressed via a \textit{two-centre} Hamiltonian \( h^\alpha \), which for a non-collinear case takes the following form:

\[
h^\alpha = c^\alpha - E_\nu + \sqrt{d^\alpha} \left( U S^\alpha U^\dagger \right) \sqrt{d^\alpha},
\]  

(1)

where \( S^\alpha \equiv S_{RL'}^{\alpha R L} \) is the spin-independent matrix of the localized structure constants, \( c^\alpha \) and \( d^\alpha \) are the matrices of potential parameters, diagonal in spinor space, \( E_\nu \) are the reference energies chosen at the centres of the respective bands, and \( U \) is the spin-\( \frac{1}{2} \) rotation matrix. \cite{18}

In practice, to make use of the recursion method, we have constructed a nearly-orthonormal representation starting from the most localized tight-binding Hamiltonian \( h^\alpha \), Eq.(1), rotated such that we obtain the hamiltonian matrix in the global coordinate system,

\[
H^\gamma = U^\dagger \left( E_\nu + h^\alpha (1 - \sigma^\alpha h^\alpha)^{-1} \right) U = U^\dagger (E_\nu + h^\alpha - h^\alpha \sigma^\alpha h^\alpha + \cdots) U
\]  

(2)

The local density-of-states matrices \( N_{R\sigma,R\sigma'}(E) = \frac{-1}{\pi} \text{Im} \langle R\sigma | (E - H^\gamma + i0)^{-1} | R\sigma' \rangle \) have been found by the recursion method with the hamiltonian \( H^\gamma \), Eq.(2). The orientation of a local spin quantization axis can be found easily (in the ASA) by diagonalising the density matrix integrated over the atomic spheres.

In the first instance, we have checked the present method on the well-studied case of fcc-Fe in order to compare the results with those calculated by the ASW method \cite{23} and have found all the results to be consistent with each other.

We have then applied the RSTB-LMTO method for 60 atom structural models for liquid Al\textsubscript{60}Mn\textsubscript{40} and Al\textsubscript{80}Mn\textsubscript{20}, and 56 and 98 atom models for liquid Al\textsubscript{84}Mn\textsubscript{14}. The structural models of these Al-Mn systems were constructed by means of a standard Monte Carlo method with bond-order potentials \cite{15}. To construct the continued fractions needed for the recursions we have used up to \( \sim 1200 \)-atom clusters built from our supercells by applying periodic boundary conditions.
The topological short range order in Al$_{60}$Mn$_{40}$ was found to be quite different from that in Al$_{80}$Mn$_{20}$: in the former we have $Z_{\text{MnMn}} = 3.38$ for the Mn-Mn coordination number, whereas in the latter $Z_{\text{MnMn}}$ is just 1.36. The analysis of bond angles shows some tendency for Al$_{80}$Mn$_{14}$ and Al$_{80}$Mn$_{20}$ liquids to have an icosahedral motif, but not for Al$_{60}$Mn$_{40}$ [15].

We have found a strong tendency for magnetic moments on Mn to have large absolute values and orientational disorder (non-collinear magnetism), so that the net magnetic moment has a very low average value (Table I). It is important to note that for c-Al$_{6}$Mn our non-collinear calculations yielded a non-magnetic state, in accordance with our previous discussion of the role of the van Hove singularity at the Fermi level in the density of states of this system [15]. All average values in the present calculations are close to our previous results [15] based on large structural models and averaged self-consistent potential parameters (Table I). Moreover, in the collinear case we have found no meaningful changes in the distribution of the local magnetic moments, although in [14] the values of the Mn magnetic moment are somewhat larger. For Al$_{84}$Mn$_{14}$ system the averages are in good agreement for small (N=56) and large (N=98) calculated cells in spite of rather few statistics for Mn in the former calculation.

The analysis of the densities of states projected onto the local magnetization axes reveals that the total electronic density of states (DOS) has a sharp peak for majority spins in all liquid Al-Mn alloys at about $-2.5$ eV below the Fermi level (Fig. 1), and a peak in the unoccupied minority spin band at about +1 eV. The local projected DOSs are similar to those calculated in our previous work [14]. The difference between collinear and non-collinear DOS grows with increasing Mn concentration (Fig. 1). We note that the shape of the majority/minority DOS reflects a strongly non-rigid band behaviour (Fig. 1) so that the rigid band Stoner model is hardly applicable to Al-Mn systems.

We have found that the non-collinear state is more stable than the collinear one, being lower in energy by about 0.025 Ry (Table I). The average value of the Mn moment in our calculation is almost independent of the manganese concentration in correspondence with the experiment [3].
In our calculations the distribution of the absolute values of the Mn moment is asymmetric in Al$_{86}$Mn$_{14}$ and Al$_{80}$Mn$_{20}$, and it is biased towards higher values, whereas the moment distribution in Al$_{60}$Mn$_{40}$ is symmetric (Fig. 2). To gain more insight into the spatial distribution of the moments on Mn we have analyzed the average cosine of the angle between Mn moments, $\cos(\theta_{ij})$, as a function of the distance $R_{ij}$ between them (Fig. 3), in conjunction with the Mn-Mn partial radial distribution function. For Al$_{86}$Mn$_{14}$ liquid the nearest neighbours are likely to be subject to a ferromagnetic exchange interaction, whereas other studied systems display a definite antiferromagnetic sign of the interaction between nearest Mn atoms which changes quickly into ferromagnetic with increasing separation. The analysis of $\langle \vec{e}_i \cdot \vec{e}_j \rangle_{Mn}$ for all Mn-Mn neighbours with separations $R_{ij}$ demonstrates a preference for antiferromagnetic alignment of distant ($4.7\text{Å} < R_{ij} < 6.1\text{Å}$) Mn moments (Table I). The behaviour of Al-Mn systems is quite different compared to Mn in fcc-Al where the exchange has a ferromagnetic sign up to the 3rd neighbours [11]: topological disorder produces RKKY exchange of random signs and, therefore, results in the random directional order of moments on the manganese atoms.

In conclusion, present calculations confirm our earlier prediction [15] that topological disorder is the main driving force for the formation of a large ($\mu_{eff} \sim 2.8\mu_B$) magnetic moment on Mn in Al-Mn liquids. This value is close to the the single-impurity limit [7], and is not sensitive to interaction with other Mn atoms in the alloy, as found recently in experiment [5]. Our results do not confirm the view that only small fraction of Mn sites in disordered system carry a moment due to a strong local environment effect, with others being non-magnetic: we have found that all Mn sites are magnetic in the disordered systems we studied (Table I).

The observed rise in magnetic susceptibility $\chi$ above the melting point in Al-Pd-Mn systems [5] is quite the opposite to what is expected from the usual spin-fluctuation theories where $\chi$ is Curie-like and, therefore, decreases with temperature [24]. This rise may be a fingerprint of Kondo unscreening with increasing temperature, but could also be a result of a variation of the moments distribution (Fig. 2) with temperature and local environment.
effects, facts which should be analysed further.

We predict that Al-Mn liquids have a random magnetic order with predominance of ferromagnetic interactions for nearest Mn neighbours, and that non-collinearity is triggered by random RKKY interaction between solute atoms of Mn in a disordered Al matrix.

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TABLE I. The results for collinear (C) and non-collinear (NC) spin configurations. $\mu_{\text{min}} : \mu_{\text{max}}$ is the interval spanned by the values of Mn moments; $<\mu_{\text{Mn}}>$ and $<\mu_{\text{Al}}>$ are the averages of the moment values on Mn and Al respectively. $\mu$ is the value of the average moment per atom. $<\vec{e}_i\vec{e}_j>_{\text{Mn}}$ is the average cosine of the angle between moments on two neighbouring Mn atoms. $E_{\text{fm}} - E_{\text{nc}}$ is the energy difference between ferromagnetic and non-collinear configurations. All the moments are in units of $\mu_B$. For collinear calculations the directions of Al moments are opposite to those of Mn moments.

|                | Al$_{60}$Mn$_{40}$ | Al$_{80}$Mn$_{20}$ | Al$_{86}$Mn$_{14}$ |
|----------------|--------------------|--------------------|--------------------|
| $\mu_{\text{min}} : \mu_{\text{max}}$ | 1.96 : 3.08        | 1.28 : 3.39        | 1.62 : 3.49        |
| $<\mu_{\text{Mn}}>$ | 2.68               | 2.72               | 2.84               |
| C              |                    |                    |                    |
| $<\mu_{\text{Al}}>$ | 0.096             | 0.048              | 0.039              |
| $\mu$          | 1.01               | 0.51               | 0.37               |
| $\mu_{\text{Mn}}^a$ | 2.87               | 3.17               | 3.29               |
| $\mu_{\text{min}} : \mu_{\text{max}}$ | 2.05 : 3.43        | 1.42 : 3.54        | 1.86 : 3.39        |
| $<\mu_{\text{Mn}}>$ | 2.74               | 2.89               | 2.88               |
| $<\mu_{\text{Al}}>$ | 0.062              | 0.036              | 0.029              |
| NC             |                    |                    |                    |
| $\mu$          | 0.27               | 0.23               | 0.08               |
| $<\vec{e}_i\vec{e}_j>_{\text{Mn}}$ |                    |                    |                    |
| $R_{ij} < 4.7\text{Å}$ | 0.22              | 0.42               | 0.13               |
| $4.7\text{Å} < R_{ij} < 6.1\text{Å}$ | -0.09             | -0.21              | -0.25              |
| $E_{\text{fm}} - E_{\text{nc}}$ (mRy) | 25                | 24                 | 26                 |

$^a$The result of collinear calculation [13]
FIGURES

FIG. 1. The spin-polarized electronic density of states for Al-Mn liquids: (a) Al\textsubscript{84}Mn\textsubscript{14}, (b) Al\textsubscript{80}Mn\textsubscript{20}, and (c) Al\textsubscript{60}Mn\textsubscript{40}. Solid line: density of states for a global quantization axis, non-collinear configuration; dot-dashed line: the same for a local quantization axis; dotted line: the density of states per spin for the collinear case.

FIG. 2. The diagram of the Mn moments distribution in Al-Mn liquids. \( \theta \) is the angle between magnetic moment and magnetization axis. Vertical line marks the centre of gravity of the distribution. Note the asymmetry of moment distribution in Al\textsubscript{86}Mn\textsubscript{14} and Al\textsubscript{80}Mn\textsubscript{20}.

FIG. 3. The cosine of the angle between two Mn moments (solid line) and partial Mn-Mn radial distribution functions (dashed line, right axis).