Detailed *ab initio* calculations of the structure and magnetic state of a metallic spin glass

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Abstract. We present for the first time a long-sought atomic and magnetic structure of one of the most well-known and studied spin-glass systems: the Cu\textsubscript{83}Mn\textsubscript{17} alloy, which is the prototype for a large class of metallic spin-glass systems. The structure has been determined from simulations based on atomic and magnetic interactions obtained from first-principles calculations. Being in perfect agreement with recent neutron scattering experiments, our results reveal the atomic and magnetic structure that exhibits a specific short-range order (SRO) and is believed to be responsible for a complicated magnetic cluster dynamics leading to the spin-glass behaviour in this alloy. The ordered phase underlying the atomic SRO is shown to have a Cu\textsubscript{3}Mn-type structure with 16 atoms per unit cell. The magnetic SRO is associated with incommensurate spin-spiral correlations.

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1. Introduction

The basic attributes of a spin glass are a quenched, or frozen-in configurational disorder of atoms on a lattice, and magnetic frustration, which implies that the interaction energy of a spin coupled to a local field is degenerate. In mean-field-based theories [1, 2], the configurational disorder is assumed to be described by a random distribution of magnetic interactions (or bonds) between sites of a fully occupied simple lattice, and such models have successfully reproduced general aspects of the spin-glass behaviour [3, 4]. However, the structure of real materials, like Cu–Mn alloys, seems to be much more complicated, and as has been pointed out by many researchers, details of the structure may play a key role in the glassy behaviour in these types of alloys [5]–[8].

The major feature of spin-glass materials, which is missing in simplified models, such as the most prominent random-bond Edward–Anderson and Kirkpatrick–Sherrington models [1, 2], is the presence of magnetic clusters. In the particular case of Cu–Mn and other noble metal–manganese alloys, neutron scattering experiments reveal quite strong magnetic correlations of both ferromagnetic and antiferromagnetic character appearing at temperatures several times higher than the temperature of spin-freezing. It is argued [3] that such magnetic clusters, persisting in the paramagnetic phase, are responsible for spin-freezing in these systems. A clear picture of the atomic and magnetic structure of noble-metal manganese alloys is, therefore, a key prerequisite for a correct understanding of these types of spin glasses.

In the discussion below, we focus on dilute CuMn alloys as the most thoroughly investigated ones among other similar systems (like AgMn, AuMn and PtMn). Numerous neutron scattering experiments have provided us with data on macroscopically averaged pair correlations, both atomic and magnetic [5, 6], [8]–[11]. According to the experimental results, the atomic configuration does not transform into an ordered state while being cooled down from higher temperatures. Instead, it forms a largely disordered state with a short-range order (SRO) characterized by a ‘diffuse’ concentration wave with wavevector \(Q_a = (1, 1/2, 0)\).

At lower temperatures, this atomic SRO modulates the spin configuration leading to the appearance of small ferromagnetic clusters. At the same time, the magnetic interactions themselves, regardless of the atomic ones, tend to arrange the spins into a spin-density wave (SDW) structure, whose wavevector \(Q_m = (1, 1/2 \pm \delta, 0)\) corresponds to a wavelength incommensurate with the period of the underlying lattice. These experimental data, along with the results of measurements on the spin dynamics, provide a very useful piece of information with regard to the behaviour of the alloy at different temperatures, but they cannot unambiguously answer the main question: what type of interactions provide such a behaviour, and what does the detailed structure originating from these look like?

In this paper, we perform a detailed analysis of the atomic and magnetic thermodynamics of the Cu_{83}Mn_{17} alloy by mapping the total energy of the alloy calculated from first principles onto classical Ising and Heisenberg Hamiltonians. In the next section, we show how the configurational and magnetic degrees of freedom can be partially separated in a natural way thus providing a firm ground for thermodynamics simulations. In section 3, where the results of the calculations are presented, it is shown that the magnetic interactions between the Mn atoms strongly favour magnetic ordering into an incommensurate spin-spiral structure. Interatomic chemical interactions, on the other hand, lead to the precipitation of an ordered Cu_{3}Mn phase containing 16 atoms per unit cell. It seems that this phase was actually left out in previous attempts to find the ordered structure satisfying the intensity pattern observed in experiments.
2. Methods

The atomic configurational energy of the CuMn alloy can be described by the Ising Hamiltonian:

\[ H_{\text{chem}} = \frac{1}{2} \sum_{i \neq j} V_{ij}^{(2)} \sigma_i \sigma_j + \frac{1}{3} \sum_{i \neq j \neq k} V_{ijk}^{(3)} \sigma_i \sigma_j \sigma_k + \cdots, \]  

(1)

where spin variables \( \sigma_i \) take on values +1 or −1 if site \( i \) is occupied by one or the other alloy component, and \( V_{ij}^{(m)} \) are the effective (\( m \)-site) interactions. The magnetic degrees of freedom coming from well-defined localized magnetic moments of the Mn atoms can reliably be taken into account by the Heisenberg Hamiltonian:

\[ H = - \sum_{ij} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j, \]  

(2)

where \( \mathbf{e}_i \) is a unit vector in the direction of the local magnetic moment at site \( i \). The problem is, thus, reduced to calculating the parameters \( V_{ij}^{(m)} \) and \( J_{ij} \) and finding the atomic and magnetic structures from thermodynamic simulations of the Hamiltonians.

In this paper, we obtain the interaction parameters from \textit{ab initio} calculations and show how the atomic and magnetic structure of the CuMn alloy can be reproduced from these parameters by performing combined Monte Carlo simulations of the Hamiltonians (1) and (2). In calculating the interaction parameters, two major issues must be taken into consideration. Firstly, at temperatures where atomic diffusion is still possible on a reasonable timescale, that is above \( \sim 300–400 \) K, the system is in a paramagnetic state. Direct calculation of such a state, especially in an alloy with a small concentration of magnetic atoms, is a formidable task. Secondly, both chemical and magnetic interactions in this system are essentially mediated by Cu delocalized s-like states. This makes it easy for any perturbation in the electronic structure to spread out over large distances. Accordingly, correct accounting for the long-range interatomic interactions and the paramagnetic state must be an indispensable ingredient of any well-defined and consistent model of the system. Both these reasons make it practically impossible to apply such approaches like the structure inverse method [12] to the system. To some extent, the problem could be overcome by resorting to the mean-field approximation [13] that indeed provides some useful predictions, but this approach is justified only for high temperatures, failing to reproduce the observed ordering tendency, as well as low-temperature magnetic correlations.

To cope with the task of calculating chemical effective cluster interactions, as well as exchange interaction parameters, we developed the screened generalized perturbation method (SGPM), based on a method originally introduced by Ducastelle and Gautier [14]. Among the advantages of the method is its ability to treat both chemical and exchange interactions, including multisite and long-ranged, on the same footing with an accuracy practically equal to that of the underlying first-principles method [15]. Besides, SGPM enables one to determine interactions in the compositionally (in the framework of the coherent potential approximation (CPA)) and magnetically (as the disordered local model) random state in a natural way, which is vital for an accurate and reliable description of CuMn spin glasses.

Electronic structure calculations of random Cu–Mn alloys were performed by the exact muffin-tin orbital (EMTO) method [16] in the CPA [17]. The calculations were done for the disordered local moment (DLM) state, which models a spin-randomly-oriented paramagnetic state [18]. 150 pair, 82 three-site and 26 four-site effective chemical interactions were calculated.
calculated by the SGPM in order to check the convergence of an Ising-type expansion of the atomic ordering energy. The intersite screening constants for the pair SPGM interactions were determined from 864-atom-supercell calculations of the Cu$_{83}$Mn$_{17}$ alloy with random distributions of Cu and Mn atoms up to the 10th coordination shell [15]. The accuracy of the representation of the ordering energy by the SGPM interactions was checked for L1$_2$, D0$_{22}$ and D0$_{60}$ (described below) structures for Cu$_3$Mn. The difference in energies between different structures obtained from the SGPM were in good agreement with direct total energy calculations (see figure 3). Magnetic exchange interactions parameters of the classical Heisenberg Hamiltonian were calculated with the aid of the magnetic force theorem formalism [19]. We checked the dependence of the exchange interaction parameters on the magnetic state by calculating them in the DLM and ferromagnetic state. They turned out to be practically the same, which means that the magnetic state in CuMn alloys is well presented by the Heisenberg Hamiltonian, and the exchange interaction parameters are independent of the local and global magnetic state. The exchange interaction parameters were calculated up to the 300th coordination shell, with only the 40 strongest contributions being included in the Monte Carlo simulations.

3. Results

In figure 1, we show the pair effective chemical interactions and exchange interaction parameters for Cu$_{83}$Mn$_{17}$ obtained from ab initio SGPM calculations at the experimental lattice spacing [20]. Both sets have a well-pronounced long-range oscillating character. This originates, as has already been mentioned, from the free-electron-like nature of the Cu s-states mediating the interactions at long distances. At short distances, $V_{ij}$ and $J_{ij}$ also exhibit a consistent behaviour: at those coordination shells where the chemical interactions lead to a repulsion between the Mn atoms, the exchange interactions are antiferromagnetic (the first and fourth coordination shells), and vice versa, attractive chemical interactions between the Mn atoms come along with a ferromagnetic character of the corresponding exchange interactions, which reflects the importance of magnetism for interatomic interactions.

In order to resolve the atomic and magnetic structures of the Cu$_{83}$Mn$_{17}$ alloy, we performed combined Ising and Heisenberg Monte Carlo simulations using the Metropolis algorithm for both atomic and magnetic calculations. The sizes of simulation boxes varied from 8 up to 24 fcc cubic cells in order to rule out boundary effects. Firstly, the atomic configuration of Cu and Mn atoms in the paramagnetic state on the underlying face centred cubic lattice is obtained at 500 K, which is a typical annealing temperature of samples in the neutron diffuse-scattering experiment for this particular alloy [9]. The resulting atomic SRO (ASRO) parameters are in excellent agreement with experimental data. This can be seen in figure 2(a), where we compare the calculated and experimental Fourier transform of the ASRO parameters.

The characteristic feature of the ASRO in Cu$_{83}$Mn$_{17}$ is a peak at $q = (1, 1/2, 0)$. The presence of this peak implies that this alloy may undergo a transition to an ordered structure, characterized by the same superstructure vector. Indeed, if the temperature in the atomic Monte Carlo simulations is decreased, one can observe precipitation of an ordered Cu$_3$Mn (hereafter referred to as D0$_{60}$) phase in the Cu matrix at about 300 K (figure 3). Relative ordering energies of the L1$_2$ and D0$_{22}$ structures with respect to the energy of D0$_{60}$ are also present in the figure. Unfortunately, it is hardly possible to observe this ordered phase in Cu–Mn alloys experimentally due to the extremely slow diffusion rate close to room temperatures.
Figure 1. Effective pair chemical (above) and magnetic exchange (below with a minus sign) interactions drawn as a function of the coordination shell number. Positive values of pair potentials correspond to repulsion of Mn atoms and negative values correspond to attraction. Note that the NN magnetic interaction is antiferromagnetic. Similar behaviour at the nearest coordination shells leads to a higher probability of finding magnetic atoms at positions where they interact ferromagnetically, thus explaining the origin of ferromagnetic clustering.

Nevertheless, the structure defines the framework for the formation of clusters of the Mn atoms influencing the magnetic properties of the alloy.

The magnetic configuration in the spin-glass state is determined from Heisenberg Monte Carlo simulations for Mn atoms distributed on the fcc lattice according to the SRO obtained in the preceding Ising Monte Carlo simulations. Extremely slow diffusion rate (with respect to magnetic relaxation processes) allows us to fix the atomic configuration of the alloy for temperatures below 400 K. Spin freezing is registered below the temperature 80 K, which might correspond to the spin glass transition, though a more thorough thermodynamic investigation is needed in order to determine the type of the transition unambiguously.

The 0 K magnetic structure of the Mn atoms in CuMn alloys obtained from the Monte Carlo simulations nicely reproduces the magnetic SRO, as can be seen in figure 2(b). The peak at $Q_m = (1, 1/2 \pm \delta, 0)$ corresponds to an SDW (more precisely, a single-$Q$ spin spiral), which is incommensurate with the underlying lattice, even so the spin-spiral long-range order is not formed. As a result, the magnetic structure of the spin-glass state represents a mixture of ferromagnetic and SDW clusters, having their own dynamics and interacting with each other.

Although the oscillating RKKY-like character of both the atomic and magnetic interactions has the same origin connected with the properties of the copper Fermi surface, there is a certain difference in the Fourier transform of the interactions, $V(q)$ and $J(q)$. Qualitatively, $V(q)$ and $J(q)$ look similar to the corresponding intensity patterns shown in figures 2(a) and (b).
**Figure 2.** Fourier transform of the SRO parameters (a) and magnetic pair correlations (b). Numerical results are shown in the bottom-left half and experimental results [9] in the top-right half of each figure. Reciprocal space vectors are given in units of $2\pi/a$. Broken lines mark boundaries of the first Brillouin zone in the (100)-plane coming through the $\Gamma$-point.

**Figure 3.** A fragment of a supercell demonstrating the ordered structure Cu$_3$Mn (D0$_{60}$). Blue and yellow spheres correspond to the Cu and Mn atoms, respectively. The structure was originally described in [21] as an ‘N$_3$M’ phase formed by two perpendicular concentration waves with the superstructure vector $q = (1, 1/2, 0)$. For ordered structures L1$_2$ and D0$_{22}$, the relative ordering energies (in mRy) obtained from the SGPM and from direct calculations are given.

| Structure | SGPM | $E_{\text{tot}}$ |
|-----------|------|-----------------|
| L1$_2$    | 3.38 | 3.25            |
| D0$_{22}$ | 0.75 | 0.75            |
| D0$_{60}$ | 0.00 | 0.00            |

As compared with the atomic interactions, there is an additional splitting of the peak in $J(q)$, which eventually brings about incommensurate spin-spiral correlations. This demonstrates that the detailed mechanisms leading to the atomic and magnetic interactions are slightly different.
A snapshot of the Cu$_{83}$Mn$_{17}$ alloy illustrating the long-sought atomic and magnetic structure of a spin-glass system is shown in figure 4. A small fragment of the simulation box is depicted. One can clearly see that the alignment of magnetic moments on the Mn atoms has a well-correlated behaviour in accordance with the magnetic exchange interaction parameters. For instance, Mn atoms at the second coordination shell tend to form ‘ferromagnetic’ clusters (see figure 4(b)). At the same time, the magnetic structure of clusters of Mn atoms connected by nearest-neighbour bonds exhibits a spin-spiral-like behaviour. Thus, the picture enables one to see clearly the way the two types of clusters are intertwined with each other.
Although our study sheds light on the structure of magnetic clusters in the system, the mechanism of their dynamics leading to spin-glass behaviour still remains an important issue to study. The problem can be partly solved if one is able to show that effective interactions between clusters give rise to dynamics similar to that of random-bond models (like in [22]) which have been studied extensively. In this sense, the behaviour of dilute metallic spin glasses could be similar to that of amorphous cluster glasses and the name ‘cluster spin glass’ might turn out to be more appropriate for systems like the CuMn alloy.

Summarizing the results, the discovered ordered phase underlying the SRO of the dilute CuMn alloy should finally dismiss the question of the atomic structure of this material in the given concentration region. In addition, this clear microscopic picture, complemented by the description of the magnetic structure, opens a way to a more accurate or, ultimately, to a complete \textit{ab initio} modelling of the bizarre behaviour of spin glasses.

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