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**Equilibrium Properties of the Ising Frustrated Lattice Gas**

Jeferson J. Arenzon (*), Mario Nicodemi and Mauro Sellitto

Dipartimento di Scienze Fisiche (**), Università di Napoli 'Federico II', Pad. 19, Mostra d'Oltremare. 80125, Napoli, Italy

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**Abstract.** — We study the equilibrium properties of an Ising frustrated lattice gas with a mean field replica approach. This model bridges usual Spin Glasses and a version of Frustrated Percolation model, and has proven relevant to describe the glass transition. It shows a rich phase diagram which in a definite limit reduces to the known Sherrington-Kirkpatrick spin glass model.

1. **Introduction**

The Ising Spin Glass transition has been discovered to describe many seemingly different phenomena, and to model real systems much beyond what originally thought [1]. The idea of introducing frustrated Hamiltonians to capture the essential physics of glasses, random media properties, evolutionary models, protein and RNA folding, granular packing, dynamics of complex flow, and many others, has grown fertile in the last years [2–10].

Recently, in this panorama, an Ising Spin Glass like model, a general version of the frustrated lattice gas, has been introduced for its new interesting Monte Carlo dynamical and equilibrium features relevant to the description of the glass transition [6,7], and with some variations has been applied in the context of phase transitions in granular packing [8].

In this paper we study the mean field equilibrium properties of such a model, adopting standard replica formalism. The system we consider is characterized by the following Hamiltonian:

\[
\mathcal{H} = J \sum_{\langle ij \rangle} (1 - \varepsilon_{ij} S_i S_j) n_i n_j - \mu \sum_i n_i - h \sum_i S_i n_i
\]  

where the lattice gas site variables \(n_i = 0,1\) have an Ising internal degree of freedom \(S_i = \pm 1\) and \(\langle ij \rangle\) denotes summation over all nearest-neighbor pairs of sites. The \(\varepsilon_{ij} = \pm 1\) are quenched random variables, \(h\) is a magnetic field applied on the system and \(\mu\) is a chemical potential for the site variables. Essentially, the model considers a lattice gas in a frustrated medium where the particles have an internal degree of freedom (given by its spin) that accounts, for example, for possible orientations of complex molecules in glass forming liquids. As stressed by

(*) Author for correspondence (e-mail: arenzon@if.ufrgs.br)
(**) Unità INFM e Sezione INFN

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Coniglio [6], these steric effects are greatly responsible for the geometric frustration appearing in glass forming systems at low temperatures or high densities. As is detailed in reference [7], this model offers a clear and intuitive picture of the mechanism leading to a glass transition, qualitatively reproducing the complex dynamical behaviour present in this regime.

The presented Hamiltonian is a natural bridge between Frustrated Percolation [6] and standard Ising Spin Glasses (SG). Indeed, this two apparently different models are obtained in two definite limits of its parameters. If \( \mu \to \infty \) and \( J/\mu \to 0 \), for energetic reasons each site must be filled and the known Ising Spin Glass is obtained; on the contrary if \( J \to \infty \) and \( \mu/J \to 0 \), generally even at \( T = 0 \) the configuration with each site filled is impossible. In this last limit only site configurations which do not close “frustrated loops”, i.e. loops of filled sites whose spins are not satisfying all mutual interactions, are allowed. This corresponds to a site Frustrated Percolation in which clusters have a further weight factor of \( 2^{N_c} \) (\( N_c \) is the number of clusters in the system). Moreover, introducing clusters à la Kasteleyn and Fortuin, this Hamiltonian may be described in terms of a site-bond correlated and frustrated percolation.

With a simple transformation, \( \tau_i \equiv S_i n_i \), this model may be changed into an Ising spin-1 Blume-Emery-Griffiths model (BEG) [11] in which only the bilinear coupling is affected by the quenched disorder \( \varepsilon_{ij} \), while the spin biquadratic term has a coupling with opposite sign in relation to the original BEG model [12] (in notation of [12], \( K/J = -1 \)) and no disorder. In the case without frustration \( (\varepsilon_{ij} = 1) \), that has also been studied in [12], the order parameters are the dilute magnetization \( m = \langle Sn \rangle \) and the particles density \( d = \langle n \rangle \). In the \( \mu \to \infty \) limit one recovers the Ising model, with \( d = 1 \). In mean field, at \( T = 0 \), \( d = m = \Theta(\mu) \) if \( \mu \neq 0 \) and \( d = m = 1/3 \) for \( \mu = 0 \). This point with density \( 0 < d < 1 \) will become an interval when frustration is introduced. Moreover, expanding for small \( m \) we obtain the equation satisfied by the critical temperature

\[
\frac{J}{T_c} = 1 + \exp \left( 1 - \frac{\mu}{T_c} \right)
\]

and one can see that this transition line is reentrant [12], effect that will also disappear when introducing frustration.

In the following sections we study the replica mean field theory of Hamiltonian (1) with a Gaussian distributed coupling. The phase diagram of the model presents several interesting regions depending on the values of \( T \) and \( \mu/J \). For highly negative values of \( \mu/J \), there is only a paramagnetic phase. Lowering the temperature at small negative values of \( \mu/J \), the system has a discontinuous transition to a spin glass phase, in which even at zero temperature the density is lower than one. Increasing \( \mu/J \), the spin glass transition becomes continuous, while the zero temperature density is still below one. This occurs up to a certain point where the density becomes unity (at \( T = 0 \)) signalling that we are approaching the Sherrington-Kirkpatrick limit. The Parisi replica symmetry breaking solution seems to hold whenever a spin glass transition is encountered.

2. Mean Field Results

We present in this section results obtained in the mean field approximation. The starting point is the calculation of the free energy \( f \) according with the replica trick [1]:

\[
\beta f = - \lim_{n \to 0} \frac{\ln[Z^n]_{av.}}{nN}
\]
where \([ \ldots ]_{av}\) stands for the average over the disorder, which we suppose Gaussian with zero mean and variance \(J^2/N\). We obtain:

\[
\beta f = \lim_{n \to 0} \frac{1}{n} \left\{ \frac{\beta^2 J^2}{2} \sum_{a < b} q_{ab}^2 + \frac{\beta J}{2} \left( \frac{\beta J}{2} - 1 \right) \sum_a d_a^2 - \ln \text{Tr}_{\{n_n, S_n\}} e^{-\beta H_{\text{eff}}} \right\} \tag{4}
\]

where the single site Hamiltonian is:

\[
H_{\text{eff}} = -\beta J^2 \sum_{a < b} q_{ab} S^a n^a S^b n^b - J \left( \frac{\beta J}{2} - 1 \right) \sum_a d_a n^a - \mu \sum_a n^a - h \sum_a S^a n^a. \tag{5}
\]

The self consistent equations for the order parameters are given by the saddle points of \(f\) and read:

\[
q_{ab} = \langle S^a n^a S^b n^b \rangle \tag{6}
\]

\[
d_a = \langle n^a \rangle \tag{7}
\]

where the average is done using the effective Hamiltonian. The overlap \(q_{ab}\) has a certain degree of dilution in respect to the parameter introduced in the SK model [17] and reduces to it in the limit \(d_a = 1\).

2.1. Replica Symmetry. — To get a general qualitative picture of the phase diagram of the system, we first made a simple replica symmetric (RS) assumption, that is, \(q_{ab} = q(1 - \delta_{ab})\) and \(d_a = d\). The free energy then reads:

\[
\beta f_s = -\frac{1}{4} \beta^2 J^2 (q^2 - d^2) - \frac{1}{2} \beta J d^2 - \ln 2 - \int Dz \ln \left[ 1 + e^{\Xi} \cosh(\beta J \sqrt{q} z + \beta h) \right] \tag{8}
\]

where the Gaussian measure is \(Dz \equiv \frac{dz}{\sqrt{2\pi}} e^{-z^2/2}\) and

\[
\Xi \equiv \frac{\beta^2 J^2}{2} (d - q) + \beta (\mu - Jd) \tag{9}
\]

The saddle point equations obeyed by the order parameters are:

\[
d = \int Dz \frac{\cosh(\beta J \sqrt{q} z + \beta h)}{e^{-\Xi} + \cosh(\beta J \sqrt{q} z + \beta h)} \tag{10}
\]

and

\[
q = \int Dz \frac{\sinh^2(\beta J \sqrt{q} z + \beta h)}{[e^{-\Xi} + \cosh(\beta J \sqrt{q} z + \beta h)]^2}. \tag{11}
\]

The effects introduced by the magnetic field will in general not be considered here and in what follows we take, unless mentioned, \(h = 0\).

To characterize the system, in Figure 1 we present some representative curves for both \(q\) and \(d\) for several values of \(\mu/J\). For large values, the system approaches the SK limit \((T_c \to J, d \to 1\) and \(q \to q_{SK}\)). For \(\mu/J > -0.56\), the system has a continuous transition \((q \sim 0)\) at \(T_c\) satisfying

\[
\frac{J}{T_c} = 1 + \exp \left( 1 - \frac{J}{2T_c} - \frac{\mu}{T_c} \right) \tag{12}
\]
Fig. 1. — The order parameters \( q \) and \( d \) for several values of \( \mu = -0.65 \) (a), 0 (b) and 3 (c). Notice the diverse behaviour of \( d \) (and \( q \)) as \( T \to 0 \) and the discontinuous transition in (a). The respective critical temperatures are \( T_c \approx 0.13 \) (a), 0.5 (b) and 0.94 (c).

Fig. 2. — The phase diagram \( T \) versus \( \mu \). The dashed line stands for the continuous transition while the solid line corresponds to the first order one (\(-0.77 < \mu < -0.56\)) and both meet at a tricritical point. In particular, when \( J = -2\mu \), \( T_c = J(1 + \epsilon)^{-1} \approx 0.27J \) and when \( \mu = 0 \), \( T_c = J/2 \).

value to be compared with equation (2). Decreasing \( \mu/J \) further, the transition line becomes first order (for \(-0.77 < \mu/J < -0.56\)) as signaled by a jump in the order parameter. At the transition line a partial freezing takes place (\( q < d < 1 \)), behaviour that has to be compared with other disordered models with discontinuous transitions like, for instance, the \( p \)-states Potts glass with \( p > 4 \) [14] and the \( p \)-spin interaction model with \( p > 2 \) [15]. We can also see from Figure 1 that at low temperature \( q \) approaches \( d \), while the actual value they assume at \( T = 0 \), where \( q = d \) (the system being fully frozen), depends on the chemical potential as can be seen in Figure 3. The point where the transition changes behavior (\( \mu/J \approx -0.56 \)) turns out to be a tricritical one when including a non zero magnetic field. The system is a simple paramagnet (\( q = 0 \)) below this region. This information is summarized in the phase diagram \( T \) versus \( \mu \) presented in Figure 2. The reentrant phase found in the case without frustration [12] is replaced here by these various regions.
Fig. 3. — The density $d$ versus $\mu$ at $T = 0$. The point for which $d = 1$ is $\mu = 1 - (2\pi)^{-1/2}$ while for $\mu < \mu_c \approx -0.77$ there is only the $d = 0$ solution.

It is interesting to study the $T = 0$ limit of this model. For $\mu$ above the point

$$\frac{\mu^*}{J} = 1 - \frac{1}{\sqrt{2\pi}} \approx 0.6$$

(13)

it is possible to see that $d = 1$ and $C \equiv \beta J (d - q) = \sqrt{2/\pi}$, results known to be characteristic of the Sherrington-Kirkpatrick SG. Something changes below $\mu^*$, equation (13), where the saddle point equations give:

$$d = \text{erfc} \left( \frac{-\frac{1}{2} C + d - \frac{\mu}{J}}{\sqrt{2d}} \right)$$

(14)

$$C = \sqrt{\frac{2}{d\pi}} \exp \left[ -\frac{\left( -\frac{1}{2} C + d - \frac{\mu}{J} \right)^2}{2d} \right]$$

(15)

These equations imply $d < 1$ at $T = 0$, as it should be in the true $J \to \infty$ limit. On the other hand, below $\mu_c \approx -0.77$, just the paramagnetic solution $q = d = 0$ is present, the transition being discontinuous (see Fig. 3), in accordance with the above phase diagram. The main novelties present in the model appear in this region where the chemical potential is sufficiently low and frustrated loops are not completely occupied ($d < 1$). The appearance of this region is an effect introduced by the disorder since in the no frustrated case, it reduces to the point $\mu = 0$.

The entropy per site is

$$s = \frac{1}{2} \beta^2 J^2 (q^2 - d^2) + \frac{1}{2} \beta J d^2 - \beta \mu d - \beta f_s$$

(16)

As $T \to \infty$, $s \to 2 \ln 2$ since our phase space has $4^N$ possible states, and at $T = 0$:

$$s_0 = -\frac{1}{4} C^2 + (1 - d) \ln 2$$

(17)
Fig. 4. — The magnetic susceptibility $\chi$ versus $T$ for $\mu = 0$ and 3 in RS. Inset: $T = 0$ susceptibility as a function of $\mu$, showing a constant value above $\mu^*$ and a maximum in the region where $d(T = 0) < 1$.

For $\mu > \mu^*$, $s_0 = -1/2 \pi$, while for $d = 0$, $s_0 = \ln 2$. Here we clearly see the signal of instability of the replica symmetric solution. The next section treats the first step of replica symmetric breaking in the Parisi scheme, leading to corrections to these results. We also obtain the point where $s_0 = 0$, that is, $\mu_0 \approx -0.026$. The reason which makes positive the replica symmetric entropy below this value is the presence of free spins when the density is lower than unity. In those sites where $n_i = 0$, the spins are free to assume any orientation, and this increases the entropy (second term in Eq. (17)). The free energy hessian eigenvalues have to be calculated in order to verify the stability of the replica symmetry solution. Doing so we obtain from the condition of positive eigenvalues, the AT line [18]

$$\frac{1}{\beta^2 J^2} > \int D\gamma \left[ \frac{1 + e^{-\gamma} \cosh(\beta J \sqrt{q^2})}{[e^{-\gamma} + \cosh(\beta J \sqrt{q^2})]^4} \right]$$

below which the replica symmetric solution is unstable. It can be verified that the above equation is satisfied nowhere below $T_c$ and, as in the SK model, here too the replica symmetric solution is unstable, although the “degree of stability” may vary with $\mu$.

The susceptibility, $\chi = \beta(d - q)$, presents a cusp at $T_c$, as can be seen in Figure 4. The zero temperature value of $\chi$, $\chi_0 = C/J$, depends on $\mu$ as shown in the inset of Figure 4. Above $\mu^*$ it has a constant value, while below it presents a maximum. As expected above $T_c$, $\chi = d/T$, depending just on the density. We might have chosen to apply $\hbar$ to all spins in equation (1) whether their sites were occupied or not ($\hbar \sum_i S_i$). In this case in the region where $d(T = 0) < 1$, the low temperature susceptibility (now $\chi = \beta(1 - q)$) would diverge as $T^{-1}$ due to the free spins which have a strong response even to a weak field.

We report here the values of other quantities in order to characterize the system and for comparison with the known SG. The internal energy per spin is

$$u = \frac{1}{2} \beta J^2 (q^2 - d^2) + \frac{J}{2} d^2 - d\mu$$

and, at $T = 0$,

$$u_0 = -JCd + \frac{J}{2} d^2 - d\mu .$$
Fig. 5. — The compressibility $\kappa$ as a function of $\mu/J$ for $T = 0.4$, 0.3 and 0.2. In the first two cases the transition is continuous and $\kappa$ presents a cusp while in the last one it has a divergence since the transition is discontinuous.

The compressibility $\kappa = \beta^{-1} \partial d/\partial \mu$ has a cusp when the transition is continuous, although presents a divergence when the transition is first order, as can be seen in Figure 5.

2.2. Replica Symmetry Breaking. — Results in the previous section have shown the instability of the RS solution and we report here the first Parisi correction to it. However, it will appear that the phase diagram sketched above in RS is not altered.

Following the Parisi scheme [1], in the first step of replica symmetry breaking (1RSB) the $n$ replicas are divided in $n/m$ blocks containing $m$ replicas. Different replicas in the same block have overlap $q_1$ while those in different blocks have overlap $q_0$. Thus, the 1RSB free energy is:

$$\beta f_1 = -\frac{1}{4} \beta^2 J^2 \left[ (1 - m) q_1^2 + m q_0^2 - d^2 \right] - \frac{1}{2} \beta J d^2$$

$$- \ln 2 - \frac{1}{m} \int Dz_0 \ln \int Dz_1 A^m(z_0, z_1)$$

where:

$$A(z_0, z_1) \equiv 1 + e^{\Xi_1} \cosh(\beta h + \beta J z_0 \sqrt{q_0} + \beta J z_1 \sqrt{q_1 - q_0})$$

$$\Xi_1 \equiv \frac{\beta^2 J^2}{2} (d - q_1) + \beta (\mu - Jd).$$

As usual in spin-glass theory, we have to maximize the free energy as a function of $q$, $d$ and $m$, and the saddle point equations are:

$$d = 1 - \int Dz_0 [A^{-1}]_A$$

$$q_0 = \int Dz_0 [B]_A^2$$

$$q_1 = \int Dz_0 [B^2]_A$$
The order parameter $q_1$ obtained with 1RSB and $q$ with RS for $\mu = 0$ and 3. Regarding $d$, we did not find any difference between the RS and 1RSB solutions, while for $q_1$, the correction is small.

$$(d \geq q_1 \geq q_0)$$

and $m$ satisfies

$$\frac{1}{4} m^2 \beta^2 J^2 (q_1^2 - q_0^2) - m \int Dz_0 \ln A + \int Dz_0 \ln \int Dz_1 A^m = 0. \quad (24)$$

Here we have defined:

$$B(z_0, z_1) \equiv \frac{\sinh(\beta h + \beta Jz_0 \sqrt{q_0} + \beta Jz_1 \sqrt{q_1 - q_0})}{e^{-\beta \ln A(z_0, z_1)}} \quad (25)$$

and

$$[X]_A = \frac{\int Dz_1 A^m X}{\int Dz_1 A^m} \quad (26)$$

The numerical solutions, which can be obtained by either maximizing the free energy or by solving the coupled system of saddle point equations, are shown in Figure 6. The density does not change in relation to the replica symmetric case, while the effect of replica symmetry breaking on $q_1$ is rather small, like in the SK model. For $m$, the behavior is analogous to the one found by Parisi in the SK model, $m = 0$ at both $T = 0$ and $T = T_c$, and have a maximum at an intermediate temperature.

In analogy with the SK model, the difference between $f_s$ and $f_1$ is only perceptible at low temperatures, although depending on the value of $\mu$, this effect becomes more difficult to notice. It can also be seen that $f_1 \geq f_s$, as expected, and that the regions with wrong curvature (negative entropy) in the RS solution are largely reduced.

The susceptibility is given by

$$\chi = \beta [d + (m - 1)q_1 - mq_0] \quad (27)$$

and the results of 1RSB are higher than the ones found in RS (see Fig. 4), as in the SK model. We have also checked that, at $T = 0$, the point where the density becomes lower than one coincides with the one obtained with replica symmetry, equation (13).

Our calculations in 1RSB confirm that the structure of the phase diagram found in replica symmetry is not altered when breaking it. The first order transition is quite similar to the one
found in other spin glass models [13–16], although the model deserves a more detailed study to clarify whether the transition is or not exactly described by one step of replica symmetry breaking. In this case the glassy behavior of the model could be rather peculiar and different from other disordered system with discontinuous transition.

3. Summary and Conclusions

In brief, we have studied the mean field theory of a simple spin glass version of the Blume-Emery-Griffiths model with standard replica formalism. This model, described by the Hamiltonian (1), bridges the usual SG, which is obtained in the limit \((J/\mu \to 0, \mu \to \infty)\), and a version of “frustrated percolation”, which is recovered if \((\mu/J \to 0, J \to \infty)\).

We have seen that the introduction of site variables \(n_i\) enrich the phase diagram of the spin glass. Specifically we have shown that the SG phase around the “frustrated percolation” limit, i.e. \(\mu/J = 0\), has peculiarities signaled, for instance, by a site density below one even in the \(T = 0\) limit. Moreover, a discontinuous transition appears for negative enough values of \(\mu/J\), which may be relevant to the description of the structural glass transition [2]. These two effects, namely the broad \(d < 1\) region around \(\mu = 0\) and the discontinuous transition, are not present in the unfrustrated model where a reentrant phase was present [12].

The transition is characterized by a cusp in the susceptibility, although for the compressibility there is a cusp when the transition is continuous and a divergence when it is first order. By comparing the results obtained with 1RSB with those found assuming symmetry, we see that we are already very near the true mean field behavior of the system, since the corrections introduced are small. On the other hand, a more detailed analysis should be done in the region where the transition is discontinuous in order to verify whether, as happens in other models with discontinuous transition [13–16], the 1RSB solution is exact.

The mean field results obtained here are in qualitative accordance with those found through numerical simulation for \(D = 3\) [7], although a simulation for the infinite range version is still lacking and it would be welcomed.

It would be interesting to study the effect of varying the couplings parameters in Hamiltonian equation (1) [19], as done in the non frustrated case in [11,12] where qualitatively different phase diagrams are so found. Also, by introducing a non zero mean in the Gaussian distribution, it might be possible to study the appearance of the reentrant phase and tune the length of the zero temperature \(0 < d < 1\) interval [19]. We expect, by the above results, that the interplay of connectivity and frustration would lead to a richer behavior than the usual spin glasses.

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References


From Modulated Phases to a Quasiperiodic Structure with a Cubic Point Group and Inflation Symmetry

P. Donnadieu (1,*), H.L. Su (2,3), A. Proult (1), M. Harmelin (2), G. Effenberg (4) and F. Aldinger (3)

(1) Laboratoire d’Etude des Microstructures, CNRS/ONERA, B.P. 72, 92322 Châtillon Cedex, France
(2) Centre d’Etudes de Chimie Métallurgique, CNRS, 15 rue Georges Urbain, 94407 Vitry Cedex, France
(3) Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft, PML, Heisenbergstrasse 5, 70569 Stuttgart, Germany
(4) Materials Science International Services GmbH, Nobelstr. 15, 70569 Stuttgart, Germany

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Abstract. — A new organisation of the condensed matter has been identified in a rapidly solidified Mg-61 at.% Al alloy. The structure is characterized by a cubic point group and quasiperiodic electron diffraction patterns showing a remarkable inflation symmetry. This new state stands as a cubic quasicrystal with an inflation symmetry characterized by ratios between inflated motifs which frequently take values related to $\sqrt{3}$ (i.e. $1 + \sqrt{3}$, $\sqrt{3}$ and $(1 + \sqrt{3})/2$). For alloys with a lower Al content (51.9 and 55.3 at.%) we identify quasiperiodic structures with a cubic point group and no inflation symmetry. These phases are similar to the incommensurately modulated structures observed in other systems (V-Ni-Si, Mo-Cr-Fe). According to the electron diffraction patterns, these modulated phases are precursor states of the cubic quasicrystal with inflation symmetry. All these phases are metastable and transform on annealing around 300 °C into the crystalline phases expected from the equilibrium Mg-Al system in this composition range.

Résumé. — Nous avons identifié dans un alliage Mg-61 at.% Al élaboré par trempe rapide un nouvel état organisé de la matière condensée. Cet état constitue le premier exemple de quasicristal de groupe ponctuel cubique avec des diagrammes de diffraction quasipériodiques ayant une symétrie d’inflation remarquable : les rapports entre les motifs inflation ont des valeurs irrationnelles reliées à $\sqrt{3}$: $1 + \sqrt{3}$, $\sqrt{3}$ et $(1 + \sqrt{3})/2$. Pour des teneurs inférieures en Al (51,9 et 55,3 at.%), nous obtenons aussi des alliages à structures quasicristallines de groupe ponctuel cubique mais sans la symétrie d’inflation. Ces phases apériodiques sont analogues aux phases modulées incommensurables identifiées dans d’autres systèmes (V-Ni-Si, Mo-Cr-Fe). D’après les diagrammes de diffraction électronique, ces phases modulées sont des états quasipériodiques précurseurs de la structure à symétrie d’inflation. Toutes ces phases sont métastables et évoluent par recuit vers 300 °C vers les phases cristallisées prévues par le diagramme d’équilibre Mg-Al dans ce domaine de composition.

(*) Author for correspondence (e-mail: donnad@onera.fr)

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1. Introduction

Since the discovery of quasicrystals in Al-Mn melt-spun alloys, some other intriguing aperiodic structures have been recently reported [1–3]. These phases (frequently called modulated phases) are characterized by a cubic symmetry and electron diffraction patterns with well-defined spots occupying aperiodic positions. Such phases can not be described as simple modulated phases because of particular extinctions. They can be understood only by referring to hyperspace crystallography [4]. Withers et al. [1] have shown that the indexation of these unusual diffraction patterns require a 6-dimensional system. Because of this 6-dimensional nature, these modulated phases can be considered as quasiperiodic structures but they differ from the known quasicrystals by two features: the non-forbidden symmetry group and the absence of inflation symmetry. Several modulated states have been observed which correspond to different incommensurability parameters [1, 5]. The occurrence of a similar phase formed in annealed steels has been recently reported by Donnadieu et al. [3]. Several features allowed to relate this modulated phase to a crystalline χ-phase, Fe12Cr7Mo3, isostructural to α-Mn [6]. As the γ-phase in the Mg-Al system is also isostructural to α-Mn, we have focused our interest on the Mg-Al system. In the composition range from 47 to 61 at.% Al the existence of two equilibrium intermetallic phases, the so-called γ- and β-phases (1) is well established [7]. The crystalline γ-phase is body centered cubic (I43m, a = 1.054 nm) and contains 58 atoms [8]. The β-phase is face centered cubic (Fd3m) with a large unit cell (a = 2.8239 nm) which contains approximately 1168 atoms [9]. The structure is ideally described with a packing of icosahedra and truncated tetrahedra called Friauf polyhedra. The unit cube contains 672 icosahedra, 252 Friauf polyhedra and 244 other coordination polyhedra. In the composition range between the γ- and β-phases, other intermetallic compounds have been reported but confusion exists until now regarding their number and identity. Near 56 at.% Al, a rhombohedral crystalline phase called ε with large cell parameters (a = 1.28254, c = 2.17478 nm [10]) is stable between ~250 and 410 °C [11].

Regarding the metastable phases formed in this composition range in rapidly solidified Mg-Al alloys, various structures have been tentatively proposed in the past by different authors [12–14] (Tab. I). For a melt spun alloy containing 58 at.% Al, the occurrence of a metastable phase, named “X phase” was observed by Kobayashi et al. [15–17]. The “X phase” was also detected for other alloy compositions [16, 17] and the diffraction electron patterns were reported. The ‘X phase” was suggested to be cubic [17] but no cell parameter has been proposed. Kobayashi et al. [15, 16] pointed out that the metastable X-type phases differ from each other by small shifts of the electron diffraction spots while the main spots were unchanged. Actually, this X-phase is analogous to the modulated phase described by Withers et al. [1].

The systematic observation of phases with increasing incommensurability parameters suggested us that there might be a sequence leading to a new quasiperiodic phase with a specific inflation symmetry. This opinion was suggested by a previous work showing the continuous transition from the approximant crystal to the quasicrystal in the Al-Li-Cu system [18]. In the present case, we expected a quasicrystal different from all the known quasicrystals since the modulated phases have a cubic point group. Therefore we have investigated the Mg-Al system for several compositions ranging from 47 to 61 at.% Al. Quenched alloys have been investigated by differential scanning calorimetry (DSC), X-ray diffraction (XRD) and transmission electron microscopy (TEM). In addition to the metastable X-phases already observed by Kobayashi

(1) The formula Mg17Al12 is generally assigned to the γ-phase though this phase has a large solubility range at high temperature (from 39.5 to 55 at.% Al between 440 and 450 °C). The β-phase is usually given the formula Mg2Al3 though β is not strictly stoichiometric and has a solubility range. The maximum composition range of β is approximately 59.7 to 61.5 at.% Al.
Table I. — Various metastable Mg-Al phases reported in the literature for alloys rapidly solidified from the melt.

<table>
<thead>
<tr>
<th>Al (at.%)</th>
<th>Description of the metastable phases and lattice parameters (in nm)</th>
<th>Equilibrium phases expected at 25 °C [11]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>no icosahedral phase [32]</td>
<td>γ</td>
</tr>
<tr>
<td>55.46</td>
<td>tetragonal $\gamma'$ $a = 1.05014$  $c = 1.01849$ [12]</td>
<td>$\beta + \gamma$</td>
</tr>
<tr>
<td>58</td>
<td>X phase [16]</td>
<td>$\beta + \gamma$</td>
</tr>
<tr>
<td>60</td>
<td>no icosahedral phase [32]</td>
<td>$\beta$</td>
</tr>
<tr>
<td></td>
<td>hexagonal $a = 0.572$  $c = 0.954$ [13]</td>
<td></td>
</tr>
<tr>
<td>60.5</td>
<td>low symmetry phase related to the icosahedral phase [14]</td>
<td>$\beta$</td>
</tr>
<tr>
<td>65.7</td>
<td>(ssAl)* + X phase +$\beta$ [16]</td>
<td>(Al) +$\beta$</td>
</tr>
<tr>
<td>70</td>
<td>(ssAl)* + X phase [15-17]</td>
<td>(Al) +$\beta$</td>
</tr>
<tr>
<td>80</td>
<td>(ssAl)* + X phase [16]</td>
<td>(Al) +$\beta$</td>
</tr>
</tbody>
</table>

(ssAl)* means: supersaturated Al solid solution

et al., we have found a new aperiodic phase with a cubic point group and inflation symmetry [19]. A striking analogy between this quasicrystal and icosahedral quasicrystals concerns the inflation symmetry: the ratios between inflated motifs frequently take values related to $\sqrt{3}$ (i.e. $1 + \sqrt{3}$, $\sqrt{3}$ and $(1 + \sqrt{3})/2$).

2. Experimental Conditions

The alloys were prepared from high purity Mg (> 99.99%) and Al (> 99.99%). A master bulk ingot (about 1 cm diameter and 5 cm height) was obtained by melting the elements in a graphite crucible in an argon atmosphere. Melting of the ingot by means of high frequency induction was repeated three times for homogeneity. Rapid solidification was then carried out using the planar flow casting method with a single copper roller. The linear surface speed of the roller was 19 m/s. The quenched ribbons thus obtained were about 1 cm width and 60 μm thickness. The composition of the ribbons was determined using inductively coupled plasma/atomic emission spectroscopy (ICP-AES) and found very close to that derived from
Fig. 1. — XRD patterns for rapidly solidified Mg-Al alloys containing 47.0, 51.9, 55.3 and 61.0 at.% Al, respectively.

the weighed elements (deviation between 0 and 1 at.%). DSC measurements were carried out using a Perkin-Elmer DSC-2C apparatus. The quenched alloys were examined by XRD at room temperature using a Philips PK 1730/10 diffractometer with CoKα radiation (λ = 0.178896 nm). TEM was carried out with a CM 20 Philips microscope operating at 200 kV. TEM samples were prepared from the 60 µm as-quenched ribbons by ion beam thinning (6 keV, 0.5 mA, 14° incidence angle).

3. XRD and Electron Diffraction Analysis

3.1. XRD. — The XRD patterns for the as-quenched samples with compositions ranging from 47.0 to 61.0 at.% Al are shown in Figure 1. For the Mg-47 at.% Al alloy, all lines of the XRD pattern can be indexed according to the crystalline γ-phase. When the Al content increases, splitting of the main lines is observed and this splitting increases with the Al-content. The XRD patterns can not be anymore interpreted referring to the crystalline structure of the γ-phase or to the ε- or β-equilibrium phases. TEM is therefore necessary to identify these structures.

3.2. ELECTRON DIFFRACTION PATTERNS. — A systematic electron diffraction study has been carried out on the same as-quenched samples. Figures 2, 3, 4, 5 display sequences of electron diffraction patterns (EDPs) having respectively the 4mm, 3m and 2mm symmetry. From Figures 2 to 5, the Al content ranges from 47 to 61 at.%. Only the samples with 47 at.% Al (Fig. 2) are crystalline in the as-quenched state and agree with the structure of the γ-phase. All the other samples exhibit aperiodic diffraction patterns. Concerning the symmetry group, the 4mm, 2mm and 3m symmetries of the EDPs indicate that all these phases have a cubic point group. In addition, for the Mg-61at.% Al samples (Fig. 5), we carried out a reconstruction of the reciprocal space by TEM using a tilt-rotation holder that confirms the cubic point group. The diffraction rows in Figures 2 and 5 have been labelled according to their respective symmetry (4-fold, 2-fold, 3-fold = A4, A2 and A3).
Fig. 2. — Sequence of EDPs for the rapidly solidified Mg-47.0 at.% Al alloy. The structure is identified as that of the crystalline equilibrium $\gamma$-phase which is described by a BCC cell with lattice parameter $a = 1.05$ nm. The labels A4, A3, A2 respectively refer to the symmetry of the reciprocal space directions. When the sample composition changes (Figs. 3, 4, 5) the EDPs show the same symmetries as those observed for the crystalline $\gamma$-phase Mg-47 at.% Al alloy.

The Mg-51.9 at.% Al and Mg-55.3 at.% Al samples (Figs. 3 and 4) show EDPs similar to the ones observed in V-Ni-Si alloys [1]. They are characterized by a quasiperiodic lattice of intense spots surrounded by satellites. The distance from satellites to the main spots is larger in the Mg-55.3 at.% Al (Fig. 3) than in Mg-51.9 at.% Al (Fig. 4) alloys. The line splitting observed on the X-ray diffraction patterns (Fig. 1) of Mg-51.9 at.% Al and Mg-55.3 at.% Al samples is thus explained: these shifts result from modulated structures having different incommensurability parameter. It means that, in the indexation frame proposed by Withers et al. [1], different incommensurability parameters should be used to describe this splitting. In the following, the Mg-51.9 at.% Al and Mg-55.3 at.% Al rapidly solidified alloys will be referred to as modulated phases by analogy with the V-Ni-Si alloys [1].
Fig. 3. — Sequence of EDPs for the rapidly solidified Mg-51.9 at.% Al alloy. The EDPs in Figures 3a, 3b, 3c respectively show the 4mm, 3m and 2mm symmetries characteristic of a cubic point group. In Figures 3a and 3b, the diffraction spots clearly occupy non-periodic positions. Note that in the EDP of Figure 3c, the aperiodic behavior consists in splitting of the diffraction spots as well as extinction of the main spots. Splitting and extinction depend on the position of the spots in the reciprocal space.

In contrast with the EDPs published for V-Ni-Si and Cr-Mo-Fe [1-3], the modulated phase EDPs studied in this work show aperiodic satellites visible up to a large reciprocal distance from the main spots. Moreover, the 4-fold EDPs (Figs. 3a, 4a) show complex patterns for large Bragg angles which are not predicted in the simulated EDPs given by Withers et al. [1]. These differences are certainly due to the exposure time. Very long exposure time (up to 5 minutes) have been here applied to check whether the reciprocal space was dense or not. The modulated phase reciprocal space does not seem dense (Figs. 3 and 4) which means that the corresponding structures are quasiperiodic but with no inflation symmetry. On the contrary, Figure 5 reveals that the Mg-61 at.% Al as-quenched alloy has a dense reciprocal space. This property is particularly obvious in Figure 5c. The dense aspect of the EDPs is due to the inflation symmetry. This is why the Mg-61 at.% Al rapidly solidified sample deserves a particular interest.
Fig. 4. — Sequence of EDPs for the rapidly solidified Mg-55.3 at.% Al alloy. As in Figures 2 and 3, the EDP sequence indicates a cubic point group. The EDPs show the same non-periodic behavior as those observed for the sequence shown in Figure 3. However, Figure 4c reveals that this state is characterized by larger splitting distances.

4. The Mg-61 at.% Al Rapidly Solidified Alloy: a Cubic Quasicrystal with Inflation Symmetry

The inflation symmetry is particularly obvious in Figure 5c but it also exists in the 4-fold and 3-fold EDPs (Figs. 5a and 5b). For clarity, Figure 6 gives a sketch of the diffraction patterns pointing out the inflation symmetry. Among the measured ratio between inflated motifs, some values are found frequently: 2.73, 1.73 and 1.36 within deviations smaller than 1%. Such ratios respectively remind of the irrational numbers $1 + \sqrt{3}$, $\sqrt{3}$ and $(1 + \sqrt{3})/2$.

We observe on the EDPs (Fig. 5) a strong structure factor which is a usual feature of quasicrystals. However, to test whether this structure does not result from twinning, dark-field images as well as nanoprobe electron diffraction have been carried out. No evidence of twinning was revealed by both techniques. The EDP taken with a 10 nanometer probe size
Fig. 5. — Sequence of EDPs for the rapidly solidified Mg-61 at.% Al alloy. The EDPs shown in a, b, c respectively have the 4mm, 3m, 2mm symmetries indicating that the point group is cubic. The 4-fold, 3-fold and 2-fold diffraction rows are marked on the EDPs by the labels A4, A3, A2. Note that the spots are not periodically arranged along each diffraction row. The EDPs display inflated motifs; the ratio between motifs are reported in Figure 6. The black arrows point out the two intense spots corresponding to distances in agreement with the X-ray diffraction pattern shown in Figure 1.

perfectly overlapped with the one taken in the selected area mode (0.5 mum). This observation rules out the possibility of twinning effects for domain size larger than 10 nm. Hence, the Mg-61 at.% Al rapidly solidified alloy appears as an example of a cubic quasicrystal with inflation symmetry.

The X-ray diffraction pattern of the Mg-61 at.% Al rapidly solidified alloy is non-indexable as a crystalline phase and shows two strong lines (Fig. 1). These features are now explained by the EDPs. Thus a few lines on the XRD patterns are not due to texture but to the strong structure factor. The two strongest spots observed by TEM are indicated by arrows on the EDP in Figure 5c and correspond to the distances: 0.240 nm and 0.250 nm (±0.004 nm) which are consistent with the two intense X-ray diffraction lines (0.2401 nm and 0.2474 nm).
5. Discussion

5.1. Quasicrystals and Non-Forbidden Symmetry. — Since the discovery of the Al-14 \%at. Mn icosahedral quasicrystal [20], numerous quasicrystals have been obtained by rapid solidification. Most of them have a icosahedral point group but quasicrystals with other symmetry group have been also discovered such as the decagonal, dodecagonal and octagonal quasicrystals [21–23]. These experimental facts suggested that quasicrystals would always exhibit forbidden symmetry. In fact, theoretically, quasicrystals are not necessarily structures with a forbidden symmetry. According to the projection method, quasicrystals are generated when the slope of the selection strip as well as the projection space is irrationally oriented with respect to the hyperspace [24–26]. Indeed, the present observations show that there is a sequence of quasiperiodic structures with a cubic point group in Mg-Al rapidly solidified alloys. To our knowledge, the Mg-61 \% Al rapidly solidified alloy constitutes the first reported example of a cubic quasicrystal having, in addition, inflation symmetry. It is worth noting that the cubic point group of this quasicrystal might correspond to a 43m space group. This is suggested by the space group of the two crystalline intermetallic Mg-Al phases close to the cubic quasicrystal, namely the \( \gamma \)-and \( \beta \)-phases. In that case, the Mg-61 \% Al rapidly solidified alloy would be an example of the tetrahedral quasicrystals predicted by Sadoc [27] and Dräger [28]. Besides, in the V-Ni-Si and Cr-Mo-Fe systems, only modulated phases have been reported. Actually, we understand now, from the present work, these modulated phases are quasicrystalline phases with a cubic point group but no inflation symmetry. The sequence of modulated phases reported by Withers et al. [1], Lu et Feng [5] as well as Kobayashi et al. [15–17] also suggest that a cubic quasicrystal with inflation symmetry exists in these systems.

5.2. Analogy with the Icosahedral Quasicrystal. — On the icosahedral quasicrystal EDPs, the inflation ratio between the spot positions are related to the Golden ratio \( \tau = (1 + \sqrt{5})/2 \). In the Mg-61 \% Al rapidly solidified alloy, the observations show that the inflation symmetry is related to the irrational number \( \sqrt{3} \). In the projection algorithm, the Golden ratio is required in order to project the six hyperspace basis vectors on the six 5-fold directions of an icosahedron in the physical space. The remarkable ratios found for the cubic quasicrystal suggest that its structure should be simply generated using the projection algorithm. Of course, the irrational number \( \sqrt{3} \) provides useful information concerning the
inflation ratio but the projection matrix as well as the dimension of the hyperspace remain to be determined.

We have proposed in a related paper [19] an indexation of the spot positions along the 3-fold axis (diffraction row labelled A3 in Fig. 5c). An excellent agreement is obtained between the calculated positions and the experimental values. However, the aim of this 2-dimensional construction was only to point out the possibilities given by the projection algorithm.

5.3. Which Origin for Frustration in a Cubic Symmetry System? — If the occurrence of the quasicrystalline state is not necessarily related to a forbidden symmetry, frustration must still be involved. Of course, a forbidden symmetry naturally implies frustration but frustration in a cubic system seems at first a paradox. The analysis of the modulated phases provides some parts of an answer.

While the crystalline β-phase stands as an approximate crystal for the Mg-Al cubic quasicrystal [19], the physical significance of the modulated phases is less clear. The diffraction patterns indicate that there is a sequence of quasiperiodic structures (Figs. 3, 4 and 5) which start with the crystalline phase (Fig. 2). So the earliest stages in the sequence should give information on the origin of frustration in these systems.

In a previous work, we have analyzed a modulated state observed in the Fe-Cr-Mo χ-phase particles formed during annealing in steels [29]. This earlier stage is characterized by a two-phase microstructure [29,30]. One phase is identified as the crystalline χ-phase (BCC, a = 0.88 nm) and the second one as an icosahedral quasicrystal. We also derived that the orientation relationship between the icosahedral quasicrystal and the crystalline χ-phase is the one already observed in the Ti-Ni system [31]. This orientation sets one icosahedral 3-fold axis parallel to the <111> direction, three 5-fold axes close to <110> directions (2° deviation), three 2-fold axes parallel to the other <110> directions. Since the microstructure has a global cubic symmetry, the icosahedral phase must display four orientational variants. According to the orientation relationship, each icosahedral variant requires angular deviations of the <110> axes which are incompatible with each other. Such geometrical frustration might be responsible for the existence of cubic quasiperiodic structure.

6. Conclusion

The cubic quasicrystal with inflation symmetry and its precursor quasiperiodic phases in the Mg-Al system reported in this paper constitute an event in the field of quasicrystalline phases for several reasons. First we observe a sequence of quasiperiodic structures with no forbidden symmetry. One element of the sequence exhibits in addition inflation symmetry. This inflation symmetry is characterized by ratios related to the irrational number √3. All these quasiperiodic structures agree with the theoretical construction by projection from n-dimensional space which does not exclude quasicrystals with non-forbidden symmetry.

The second interesting aspect is the sequence of quasiperiodic structures leading to a state with inflation symmetry. The analysis of the earliest stages provides some basis to understand the origin of frustration in a cubic structure. This analysis points out the particular role of crystals with icosahedral motifs belonging to the so-called Frank-Kasper structures. The crystalline approximants of the icosahedral quasicrystals show icosahedral motifs which are oriented with the natural cube/icosahedron orientation relationship. Such relation allows only one type of variant. On the contrary, in most complex Frank-Kasper phases (α-Mn, β-phase...), the icosahedral motifs have several orientational variants in the cubic cell. This feature might lead to quasicrystals with non-icosahedral symmetry.
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