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Phase diagram for mixed ternary alloy from evolutionary optimization

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Abstract

There is an increasing interest in studying still more complicated magnetic systems. A group of ternary mixed alloys is, among them, a point of interest for as well historical as scientific reasons. The most known material belonging to this group is the famous pigment - Prussian blue. The Prussian blue analogues may be characterized by special properties, like the existence of compensation points or different magnetic phases. It is also a computationally hard problem due to a large number of possible combination of states. In this work I present the results of ground state calculations for Prussian blue analog with A lattice occupation 0.66 and $p = 0$ which is the simplest model. The phase diagram presented show dicrepancies with results presented earlier by other groups coming from the lower total energy obtained in the evolutionary computation.

1. Introduction

The applications of heuristic optimization method of Evolutionary Algorithm in the physics of magnetism may be divided into two groups. In the former paper [1,2] I presented the use of metaheuristic optimization for the thermodynamic study of simplest system considered in the frame of atomisitic spin description – the Ising model. For such a problem the crucial thing is to calculate the entropy of sample which has to be calculated only from the configurational properties of sample.

Here I am going to present the results of EA optimization adapted to the problem of so called "ground state searching". In such studies we omit the value of temperature and consider only those results which directly follow the formula describing the energy of system. It is well known that for a lot of magnetic systems its minimal energy can be either achieved analytically or using classical methods like the one of the gradient-based local optimization techniques. As an example one can show here the above mentioned two-state Ising model with the nearest neighbour interaction and without temperature. In this model the hamiltonian may be presented as follows:

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$$H = -J\sum_{nn}\mathbf{S}_i\mathbf{S}_j\,, \tag{1}$$

where H is the total energy of system, J the exchange integral characterizing the strength and character of interaction. The neighbouring spins $\mathbf{S}_i$ and $\mathbf{S}_j$ have the same modulus but may be directed either up or down thus having +/-1 value. One can notice easy that for positive J value the most energetically favorable is the configuration where all spins are ordered parallel. This situation corresponds to the well known physical property of ferromagnetism. Analogically, the negative exchange integral would lead to the antiparallel positioning which has the physical meaning of antiferro- or ferrimagnetic ordering. Such a simplest sample was a subject of study of Anderson and coworkers [3] which was the first attempt to the magnetic problems with the help of evolutionary methods. This first paper was indeed some kind of benchmark showing that magnetic problems formulated in the natural language of genetic algorithms may be analysed with them and can produce correct results.

The further considerations concerned more elaborated structures mainly spin glasses [4,5] which are characterized by different lattice structure, the same spin values but randomized exchange constants.

Here the calculations for the ternary alloy magnetic will be presented. In the next part of this paper I will present some physical objectives which motivate the interest in such material but one should underline the algorithmical possibilities connected to it. Due to its complication following as well wealthy of interactions between different spins as randomization of different spin kinds or vacancies positions in two sublattices it is characterized by the large number of possible configurations.

In the paper there will be presented the results of phase diagram calculations which show the dominant phase in various areas of space whose coordinates are the hamiltonian parameters. It ill be shown that the results assuming the same magnetization of all the same spins belonging to the whole sublattice are not the energetically optimal ones.

2. Model

The interest in mixed ternary molecular magnetics comes from the study of magnetic properties of prussian blue analogs. Among them one should list especially: antiferro coupling between nearest neighbours, hysteretis characteristic of soft magnets and the existence of compensation temperature in which all spins are flipped [6]. In this paper we will follow the system characteristics and description introduced in [7]. In this work the authors presented the phase diagram for the considered structure with the assumption that all spins of the same type have the same magnetization. Every time, when we will write about the analytical result we will refer to this paper.

The crystallographic structure of analysed materials clearly shows two interpenetrating fcc structures forming in common the sample with all simple cubic positions ready to fill. The interaction between the neighbouring spins is strongly influenced by the existence of cyanide (CN) bridging ligands which are the main element responsible for the above mentioned magnetic properties. The problem is that both sublattices, usually called "A" and "X" have some individual properties.

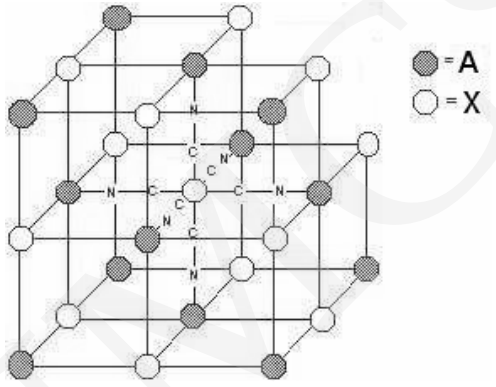


Fig. 1. The crystallographic structure of prussian blue analog with two interpenetrating lattices visible

In the case of A structure it is characteristic that some positions are empty. This feature is described by the N_A factor relatively to the fully occupied X sublattice. For the system studied N_A=2/3. In the X place there may be one of two atoms B or C. The stoichiometry of this sublattice is given by the p parameter, where

$$p = \frac{N_B}{N_X} = \frac{N_B}{N_B + N_C}. \tag{2}$$

In our case p = 0 is assumed, so indeed we take into account only the simplest structure with just two different spins.

The value which undergoes minimization is the total energy of system. It is described by hamiltonian of the form:

$$H = -\sum_{nn} J_{ij} \mathbf{S}_i \mathbf{S}_j - D \sum_i \mathbf{S}_i^2 . \tag{3}$$

Comparing it with formula (1) one can notice two distinguishable differences. The form of the first term changes due to possibility of X position occupation with two different spins what has to be formally denoted in this way. The second term is so called single ion anisotropy and certainly prefers greater spin values.

The values of spins are assumed the same as in [7] in order to describe in the best way the real structure of prussian blue $KFe^{III}[Fe^{II}(CN)_6]$. The moduli of successive spins are equal to 3/2 (A), 1 (B) and 5/2 but due to their orientation in

space in calculations we have used only the z-component which for every spin can be equal:

$$S_A = \left\{-\frac{3}{2},-\frac{1}{2},\frac{1}{2},\frac{3}{2}\right\}$$
$$S_B = \{-1,0,1\} \tag{4}$$
$$S_C = \left\{-\frac{5}{2},-\frac{3}{2},-\frac{1}{2},\frac{1}{2},\frac{3}{2},\frac{5}{2}\right\}$$

The above listing, in connection with some requirements coming from the simulational needs can give some estimation of the complexity of problem. In order to apply the periodic boundary conditions the edge size has to be even in all dimensions. Having an occupation factor for A sublattice 2/3 we have to choose value divisible by 3. The smallest acceptable size L_X=L_Y=L_Z=6 leads to the total number of 216 cell positions, 108 of them being the X ones (all filled), 108 the A ones (72 filled). Taking into account possible values of z-component and the distribution of spins in A sublattice we obtain a value about 10^{156} as a number of possible configurations of system. Certainly this number is overestimated by neglecting the recurrence of structures due to translations or rotations but even its quite significant decrease remains still too large to consider using eg. configurational space sweeping.

The values from formula (3) are presented in the relative scale:

$$J_{AB} > 0 \quad J_{AB} = 1$$
$$J_{AC} < 0 \quad R = \frac{|J_{AC}|}{J_{AB}} \tag{5}$$
$$D > 0 \quad d = \frac{D}{J_{AB}}$$

This means that AB interaction is ferromagnetic and AC is antiferromagnetic. For the sample considered here with only C type spins we expect antiparallel ordering in both sublattices

The fundamental problem when talking about magnetic sample optimisation is the representation and connected to it forms of genetic operators. The classical genetic algorithm dealt with binary coding of any problem which was almost ideal for studying the magnetic phenomena which can be described using only two possible spin states. The Ising model belongs to this group. In our case the situation is more complicated because we have to describe the system where in different positions there can appear a spin with z component taken from a different set. Therefore first of all neither binary nor floating point representation was used but the single spin is coded using the structure which encompasses as well the type of the spin as its value and position in the sample. With this model we can propose two possible forms of chromosomes. In the first of them which

we call "position oriented" spins are ordered just like in the sample. As a main advantage of this approach one has to call the surviving of "good" schemes in the process of evolution. It means that local structures, locally optimal can be hardly destroyed especially during the offspring production in the crossing phase. Such a condition is often required in physical application of metaheuristics, as an example one can list cluster structure minimization [8]. On the other hand, this approach has one major drawback, it breaks the stoichiometry of both subsystems. Then one has to include a procedure which could improve it by adding, removing or replacing necessary spins. It is obvious that this inclusion can also damage some promising spin clusters.

The second type of chromosome organization, called "spin oriented" is the one in which all spins of the same type are located together and the value undergoing evolutionary operators is (except certainly for spin value) its position in the sample. This allows us to keep constant stoichiometry but needs another crossover method. The method applied here is the "Partially Mixed Crossover" characteristic of course-type problems where the sequence of steps is the crucial problem (like eg. TSP).

Taking into account some general observations from cluster minimization we tried also to use two forms of mutation operator. The earlier attempts showed that sometimes it is profitable to use the local optimization, so the first mutation algorithm leads to the choice of spin which in the moment minimizes the energy of interaction with the adjacent ones. In the second method we just sample randomly the new value of spin among those possible for this type.

We use some basic and well known procedures of evolutionary algorithm like roulette wheel as the selection mechanism for offspring production. The parameters like population size, crossing probability, mutation probability were tested during different runs of procedure. The only interesting information may be that small population sizes are more efficient than big ones which can confirm the fact that diversity of population is not correlated with population size. Finally, the fitness function is the well known form

$$fit(\Omega) = \exp\left(-\alpha \frac{G(\Omega) - G_{\min}}{G_{\max} - G_{\min}}\right), \tag{6}$$

where α is the parameters responsible for elitism of model.

3. Results and conclusions

As the first step we tried to reproduce the results presented in the earlier mentioned analytical paper by Bobak et al. [7]. The phase diagram obtained by them with the assumption about the same magnetization of all spins in sublattice is presented in fig. 2. Three phases for different (R,d) regions are visible, all of them leading to the antiferromagnetic ordering which is expressed as the reverse signs of both spin values.

The energy minimization was initially performed for the selected (R,d) pair chosen in the well defined region of phase diagram. The reason was to find the best combination of representation/operators. The best means those leading to the global minimum in the greatest number of independent runs. Finally, the "spin oriented" model without local optimization implemented during the mutation was selected.

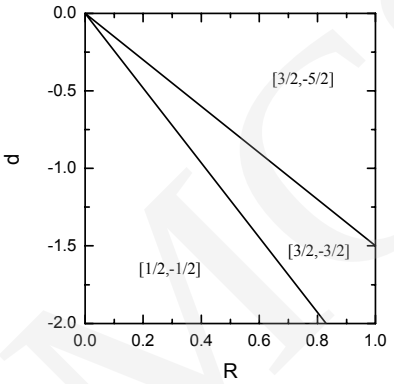
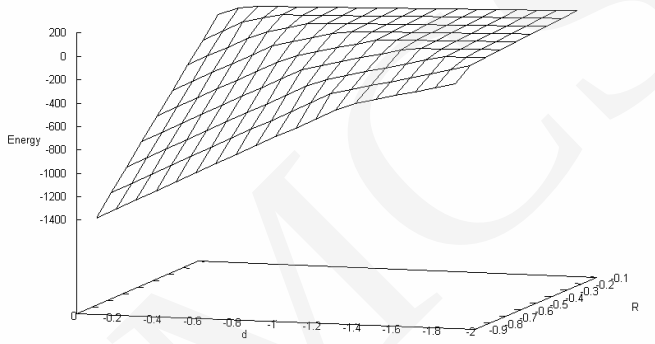


Fig. 2. Phase diagram for ternary alloy as calculated in [7]

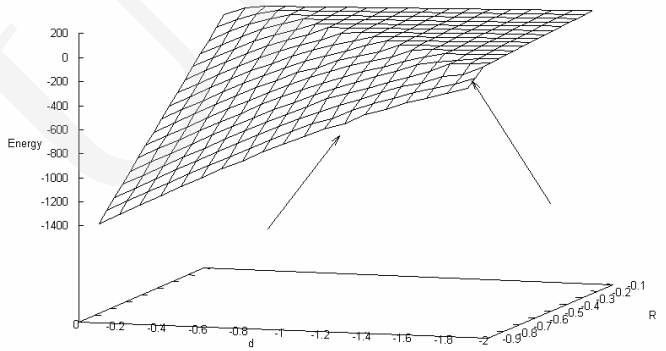
Because our calculations may be made on the discrete grid in fig. 3 there is presented a view of energy dependence on the R and d parameters. The phase change appears here as characteristic edge modifying the gradient of energy surface. The comparison of fig. 2 and the upper plot of fig. 3, done for analytical results, shows exactly the same plot. Even quite small density of points in which the energy was calculated reproduces distinctly the character of surface. The plot obtained with the evolutionary algorithm is very similar but not the same. One can notice a little perturbed phase boundary and some dips, two of them are pointed by arrows. These differences especially when confirmed by the numerical comparison suggest that there exist states for which total energy is lower than calculated using the assumption of 'pure' state ie. the same spin value of whole sublattice.

This effect is very clearly visible on the magnetization plot shown in fig. 4. The grid used in calculations makes it impossible to present the detailed structure with the exact shape of phase boundary but the existence of three separable phases is obvious. Please note that the plots in fig. 4 are made in a different perspective from those in fig. 3 but the viewpoint was selected in order to show the main features of individual plot. Here the comparison of (a) and (b) plots show significantly greater discrepancies than former one. First of all, it turns out that almost invisible energy differences can produce meaningful structural changes. In the 4b plot there are observable plateaus with magnetization values different from pure structures. Extremely unexpected is the

situation for small |d| and large |R| where (3/2,-5/2) phase should occur. This pure phase is visible only in a very narrow region around the corner of diagram. It seems that transition between the states takes place through some well defined intermediate states. From the physical point of view this result is very interesting and needs more study especially with the exact structural analysis including the visualization of possible internal low energy structures.



a)



b)

Fig. 3. The energy plot for ternary magnetic alloy shown on the grid with $\Delta R = 0.05$, $\Delta d = 0.1$; (a) analytical, (b) from evolutionary computation

From the numerical point of view, one should underline numerical hardness of problem. The roughness of as well potential energy surface (fig. 3) as magnetization (fig. 4) is a result of the problems in reaching global optimum by the algorithm. For every (R,d) point the optimization was performed 30 times and was 25 thousand generations long. Even for such a great number of repetitions the result is not guaranteed as being the minimum one. Generally, it may be estimated that for about 7.5% points, the result obtained was worse than the analytical one thus giving a certainty that global optimum was not obtained.

There is, however, the positive information that about 45% of calculations lead to the value better than shown in Bobak's work.

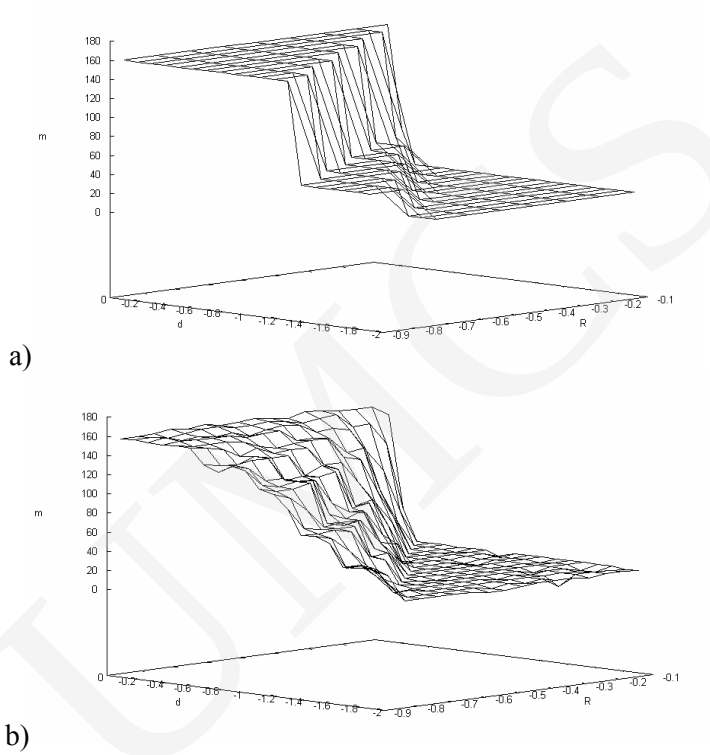


Fig. 4. The magnetization plot for ternary magnetic alloy shown on the grid with $\Delta R = 0.05$, $\Delta d = 0.1$; (a) analytical, (b) from evolutionary computation

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