Average magnetization of quasi-binary solid solution of magnetic and non-magnetic ions

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Abstract. The paper describes features of calculating the magnetization of solid solution based on statistical approach on the example of a one-dimensional crystal. Calculations are made in approximation of Weiss effective field. The result shows the error of the third Gilleo hypothesis, which is still widely used to forecast the magnetic properties of solid solutions.

1. Introduction

The need to study the properties of solid solutions in order to obtain new materials with electrodynamic characteristics capable of solving applied problem seems quite relevant. For a specific case of complex oxides with perovskite structure simultaneously exhibiting nonlinear properties of ferroelectrics and magnetically ordered media, this need was justified by Smolensky et al in [1]. However, the theory of magnetic properties of solid solutions of magnetic and non-magnetic atoms on the nodes of one sub-lattice was built even earlier in the works Gilleo and Goodenough [2–4]. In this case, the need to develop such theory is associated with the construction within molecular engineering of multicomponent ferrite spinels and garnet ferrites widely used in communication means operating within the centimeter wavelength range. In work [2], three hypotheses were advanced when calculating the temperatures dependence of magnetic phase transition (PT) on the concentration of solid solution components. The first one assumed that only those magnetic atoms (ions) whose “closest neighbors” have at least two magnetic atoms (ions) contribute to the formation of the long-range magnetic order in crystalline solid solutions of magnetic and non-magnetic ions. In this basic postulate of Gilleo and Goodenough’s theory there are some uncertainties that manifest themselves when applying the theory to both ideal and real crystals. Ferrites are multicomponent oxides containing both magnetic ions of 3-d and 4-f metals and non-magnetic ions (Zn, Si, Al...) as structure-forming agents. Elementary cells of ferrites have quite complex structure, and due to proximity of ion radii different ions with a certain probability are often placed in the structure according to the same system of correct points of a degenerate structure [5]. It is these features of the structure of ferrites that give ferrites the name solid solutions. Besides, magnetic ions in oxides are positively charged and their closest neighbors in the equilibrium structure of the dielectric or semiconductor are always negative

¹ For short let us call the transition metal atoms, the exchange interactions between which are responsible for phase transitions to magnetically ordered states simply “magnetic atoms”. The atoms of other elements placed on the same sub-lattices in a crystal as magnetic atoms are referred to as “non-magnetic atoms”.

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ions. It is the negative ions that provide the indirect exchange interaction between magnetic ions, i.e. determine the structure of the existing magnetic order. Moreover, the exchange interaction through the p-electrons of oxygen (p-ion) is most severe if the center of the oxygen ion is located on a straight line connecting the centers of magnetic ions. Thus, the indirect exchange provided by oxygen ions is sharply anisotropic, so the number of closest neighbors also depends on the structure of the ligand. Therefore, the above words “nearest neighbors of magnetic ions” are taken in quotation marks and require clarification. It shall be noted that the first Gillo hypothesis for use without reservations should be reformulated. For example in the form of a statement that the highest magnetic PT temperatures are to be expected in substances with a paramagnetic phase structure collected from ligands with highly symmetrical (weakly distorted cubic) structure and the maximum possible magnetic ion density in the structure. In this formulation, the hypothesis is well supported by the experiment [6, 7].

The second hypothesis of Gillo and Goodenough’s theory is that all magnetic atoms, among which the closest neighbors are 2, 3, 4, etc. magnetic atoms, equally contribute to the formation of the long-range magnetic order. This hypothesis does not seem very convincing. Indeed, for general reasons, it is clear that the more bonds supporting ferro- or ferrimagnetic ordering of magnetic moments of neighboring atoms, the stronger the effective field must be, and accordingly the transition temperature to the magnetically ordered state is higher. However, the phenomenological nature of Gillo and Goodenough’s theory offset all advantages in predictions of a theory based on the notion of the number of real connections between magnetic atoms. The questionable claims of the second hypothesis and its obvious disadvantages would necessarily manifest themselves if a real microscopic theory of physical properties of the condensed state of matter, in particular perfect crystals, were built. Such theory should take into account polyatomic interactions and abandon the approximation of a self-consistent field. In the approximation of the self-agreed or effective field [6, 8], the adjustable parameters are used to predict the magnetic transition temperature, the values of which are selected so that the responses of the theory correspond to the experiment. The disadvantages of Gillo and Goodenough’s theory are being addressed by modern researchers using quantum chemistry models [9–11]. In particular, recent works rely on the approximation of DFT in the form of “ab initio” [7]. Two provisions should be taken into account when assessing the results thus obtained. First, the DFT method relies on the approximation of a self-consistent field when selecting electronic wave functions. Thus, the use of DFT approximation does not remove objections to disadvantages of the approximation of a self-consistent field, and the closely related extremely coarse monatomic approximation. Apart from the above noted loss of differences between the number of links or the multivariate of the task, the approximation of an effective field with necessity leads to the loss of differences between predicted ordered structures. The work [12] gives an example where the crystal structure of the ordered phase predicted in the approximation of the self-agreed field is hexagonal, while the cubic structure is predicted in the more complete consideration of the relation dimension. The fact that the example relates to PT ordering rather than magnetic transitions is not essential to approximate a self-consistent field. Indeed, in the approximation of a self-consistent field, there is an unambiguous relationship between these two types of orders [6, 8]. It should also be borne in mind that the true Hamiltonian of interatomic interaction leading to PT is always unknown. Thus, the work [13] discusses in detail the relationship between the interatomic exchange interactions and the formed exchange interaction of the respective magnetic sub-lattices. Even from such a simple example we see a complex dependence and ambiguity of such connection. In [12], a specific example discusses the problem that arises when predicting Hamiltonian-based properties limited by the condition of accounting for not more than tetratomic interactions.

The second hypothesis of Gillo and Goodenough’s theory proved to be the main obstacle to the application of the theory to solid solutions (alloys). There are few pure metals that have the properties necessary to solve the applied problems. The difficulty arises from the fact that the uniformity of the solid solution with necessity is broken on an atomic scale. Thus, in an ideal binary solid solution, each lattice node can only be occupied by one atom – A or B. This means that each lattice node has its own
individual surroundings, which may be described using statistical methods. However, the statistics of the distribution of atoms in the solid metal solution is unknown. All statistical methods are based on certain assumptions about interatomic interactions. If atoms do not interact at all, their distribution on lattice nodes in a binary solid solution is determined by binomial distribution. The presence of interatomic interactions results in a difficult to control change of distribution. Therefore, all general statistical methods prove powerless in the study of properties of specific solid solutions. We can either justify the intended distribution or try to find basic distributions by which any pre-determined distribution in the ensemble of interacting particles could be decomposed. This way was proposed in the work by Kikuchi [14]. In [15], this method was considered for more accurate definition of the distribution of atoms in the solid solution of ions Fe$^{2+}$–Nb$^{5+}$ in ferroelectromagnet PbFe$_{1/3}$Nb$_{2/3}$O$_3$.

2. Methods and materials

1. This paper describes an example of a solid solution model of magnetic and non-magnetic atoms distributed across the nodes of a one-dimensional chain. It is shown that the third Gilleo hypothesis does not correspond to the relationship $T_c$ and $c$ obtained within the framework of approximation of the self-agreed field under any modification of hypotheses expressed in [2]. The work also illustrates some features of the theory of spontaneous magnetization and magnetic PT in solid solutions. It is noted what type of experiments would help to establish a link between the conditions of occurrence of the long-range magnetic order and the distribution of magnetic and non-magnetic ions at the nodes of a crystal lattice for specific solid solutions, including partially ordered solutions. The following calculations are made assuming the applicability of the self-agreed Weiss field approximation [6, 8].

It is known that self-consistent field models are not applicable to: 1) the description of PT between different magnetically ordered states [6, 8]; 2) the description of stable existence of complex magnetic structures [12]. The listed prohibitions on the applicability of the approach of a self-consistent field are due to the fact that this approach only takes into account paired interatomic interactions. The more nonlinear components of the non-equilibrium potential $F$ are related to the configuration entropy [12] and are characterized by a symmetry group, the order of which is $r!$. Here $r$ – number of nodes of a primitive lattice of the magnetically ordered phase of a crystal, where magnetic atoms can also be placed. Typically, these $m$ nodes are equivalent in the paramagnetic phase of a crystal if the solid solution is not characterized by a distant order in the spatial distribution of magnetic and non-magnetic atoms.

Let the distant order in the spatial distribution of the different grades of atoms that make up the solid solution also exist in the paramagnetic phase. Then $m$ is the total number of nodes belonging to different sub-lattices available for settlement by magnetic atoms in the paramagnetic phase that entered the primitive cell of the magnetically ordered phase. Let, for example, PT in magnetically ordered state be accompanied by multiplication of crystallochemical primitive cell by 6, 8, etc. Let us also suppose that a primitive cell in a disordered state contains just one node available for filling with a magnetic and non-magnetic atom. Then the symmetry of nonlinear components of the non-equilibrium potential in the approximation of the self-consistent field is described by permutation groups $G_6$ and $G_8$, the order of which is $6! = 720$ and $8! = 40320$, respectively. It is clear that the set of stabilizers of groups $L$ determining the symmetry and structure of ordered phases with full consideration of symmetry of crystal and order parameter does not coincide with the set of stabilizers of the group of symmetry of non-equilibrium potential in approximation of self-consistent field at “complex” orders [12]. In this regard, we will assume that as a result of magnetic PT in a given one-dimensional crystal one of two magnetically ordered states occurs: ferromagnetic or simplest antiferromagnetic.

The ferromagnetic state of a solid solution implies that the interatomic exchange interaction between two magnetic atoms placed on adjacent nodes of a chain favors the parallel direction of their magnetic moments. The simplest antiferromagnetic ordering implies that the exchange interaction between the nearest neighbors makes the antiparallel direction of their magnetic moments the most probable. We neglect the interaction with more distant neighbors in the consideration below, which
reduces neither the commonality of consideration nor the interesting results for our purposes obtained in the approximation of a self-agreed field.

We consider the crystal structure in the form of a one-dimensional chain to make some claims clearer without using bulky formulas. Let us emphasize that it is the approximation of the self-agreed field that allows considering magnetic ordering on a one-dimensional chain of a solid solution of magnetic and non-magnetic atoms while taking into account the interaction of only the nearest neighbors. It is known that the exact solution of the statistical problem in this case does not allow any ordering [16]. In the approximation of a self-consistent field, the results for crystal lattices of different dimensions differ only quantifiably. For purposes of illustrating the error of the Gilleo hypothesis, this difference is insignificant.

2. An arbitrary linear chain assembly filled with magnetic and non-magnetic atoms can be present in six structurally different configurations. In three of them this unit is filled with the magnetic ion, and in three – non-magnetic ion. Configurations differ in the number of closest neighbors creating an efficient magnetic field on this node. There may be be 0, 1, or 2 of such neighbors. The second variant (one magnetic neighbor) turns out to be symmetrically twice degenerate.

In the considered model, only two of the six configurations in the distribution of the three atoms on adjacent lattice nodes can contribute to the ensemble average magnetization of an arbitrary lattice node. These are configurations in which a magnetic atom sits on a node, and at least one adjacent node is occupied by a magnetic atom. Let us denote the probability of filling an arbitrary node of a one-dimensional chain with non-magnetic atoms \( p \). Then the probability that one magnetic and one non-magnetic atom may be in the chain next to a node filled with a magnetic atom is

\[
P = W_2 \cdot \exp\left(-\beta \chi^{-1} m\right) / Z_{m2},
\]

here, \( \chi^{-1} \) – inverse atomic magnetic susceptibility that can be written through Lande factor [18] to approximate a free atom or through crystal field operators in the case of an atom in a crystal lattice [18]. The “magnetic” part of the statistical sum of the considered structural configuration in the approximation of the self-consistent field:

\[
Z_{m2} = 2\cosh(\beta \chi^{-1} m).
\]

Finally, we get the average magnetic moment of the magnetic ion

\[
m = 2p \cdot (1-p)^2 \theta\left(\beta \chi^{-1} m\right) + (1-p)^3 \theta(2\beta \chi^{-1} m).
\]

Accordingly, in (3) the temperature of the second PT type in magnetically ordered state is determined by the ratio:

\[
1/\beta = k_B T_c = 2(1-p)^2 \chi^{-1}.
\]

3. Let us discuss the consequences (2)–(3). First of all, let us note that the result (2)–(3) is recorded in the form of dependence \( m(p) \), where \( p \) – probability of location of non-magnetic ions in places of nearest neighbors. This representation of the result of the calculations makes it possible to determine the dependence of the average magnetization on one crystal unit and the transition temperature to magnetically ordered state on the degree of ordering of arrangement of magnetic and non-magnetic ions, and shows the way of generalization of this result in case of three-dimensional crystals. Thus, in
the case of completely disordered distribution of magnetic and non-magnetic atoms along the nodes of the chain, the calculations make it possible to obtain a ratio that can be tested experimentally: $T_c \sim (1-c)^2$, where $c$ – concentration of non-magnetic ions of atoms.

Let us suppose by analogy with the first Gilleo hypothesis that only those magnetic atoms, which inner circle has two magnetic atoms, contribute to the establishment of the magnetic order. Then, from (3)–(4) we get

$$m^* = (1-p)^3 h(2\beta\chi^{-1} m);$$

$$k_B T_c^* = 2(1-p)^3 \chi^{-1}.$$  

Therefore, Gilleo hypothesis of the number of closest magnetic neighbors that make the magnetic ion an active participant in the formation of the magnetic order significantly affects the dependence $m(p, T)$ and $T_c(p, T)$ obtained in the approximation of the self-agreed field. Thus, if the distribution of magnetic and non-magnetic ions is completely disordered and there must be at least two magnetic neighbors, then in the model under consideration we obtain $T_c \sim (1-c)^3$, which is qualitatively different from the previous result $T_c \sim (1-c)^2$.

To illustrate the delicacy of the question on the necessary number of connections to neighboring magnetic ions so that an arbitrary lattice assembly filled with a magnetic atom can belong to an infinite magnetic-ordered region, let us give one result of the flow theory (Fig. 1, 2) [19]. Let lattice nodes filled with magnetic atoms be randomly distributed in space. For example, this is possible in solid solutions, where chaotic displacements of atoms are caused by stochasticity in the distribution of solution components to nodes of the “middle lattice” or otherwise to the nodes of the “virtual crystal” with idealized structure. Let the radius of exchange interaction of magnetic atoms with other atoms be equal $R$.

**Figure 1.** Dependence of $m(T)$ in disordered quasi-binary solid solution of magnetic and non-magnetic ions of $Fe_{1-p}(Nb, Sn)_p$ type for cases where the establishment of a magnetic order in a chain involves: 1 – all magnetic ions, 2 – only those magnetic ions that have two magnetic neighbors

**Figure 2.** Dependence of magnetic transition temperature on probability of non-magnetic neighbor of magnetic ion
Due to the mechanism of indirect exchange through electrons the conductivity $R$ can significantly exceed the distance $a$ to the nearest neighbors in the correct lattice. Under these assumptions, an arbitrary magnetic atom can belong to an infinite cluster formed of magnetic atoms only if the average number of nodes ($k$) occupied by magnetic atoms and falling into radius sphere $R$ is greater than 2.5–3 (greater accuracy at numerical experiments on the final number of nodes cannot be obtained [19]).

This result is interesting because as part of the approximation of a self-consistent field or any other model approximation when solving the dependence problem $T_c(p)$ it is impossible to establish how many exchange magnetic connections between a given ion and its closest neighbors must be broken by non-magnetic atoms so that the magnetic atom does not participate in collective effect of establishing magnetic order. However, the answer to this question can be obtained experimentally by comparing the measured dependencies $m(T, p), T_c(p)$ and $(dT_c(dp) = \Psi(p_0)$ with those obtained from theories implying a different minimum number of broken bonds.

3. Conclusion

Finally, in two and three-dimensional crystals, apart from the number of bonds of a given magnetic atom with magnetic atoms located in the nearest environment, it is necessary to further consider the conditions of propagation (“flow”) of exchange interactions to macroscopic regions of a crystal. This circumstance will make it possible to establish a lower limit of magnetic ion concentration, at which it is still possible to transition to a magnetically ordered state.

Acknowledgment

The study was carried out within the framework of the basic part of the State Task of the Russian Ministry of Education and Science 3.6439.2017/8; topic: No. 3.6386.2017/BC and 3.6439.2017/8.

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