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STATISTICS OF Ni-Ni BONDS IN Ni-BASED TERNARY SOLID SOLUTIONS WITH NON MAGNETIC ELEMENTS AND THEIR MAGNETIC BEHAVIOR

Ioan Cosma, Eugen Culea, Radu Fechete, Simona Nicoară

Department of Physics, Technical University, Str. Daicoviciu-15, 400020 Cluj-Napoca, Romania

Abstract
The drop of ferromagnetic moment in the ternary solid solutions $Ni_{1-x-y}Cu_xD_y$, (D= Zn, Si, Au, Al) is analyzed in terms of the statistical model of the environment dependent moments. This probabilistic model shows that the disappearing of one Ni atom ferromagnetic moment can be assigned to the replacement of at least four Ni-Ni bindings, out of twelve, in pure nickel. This paper aims at discussing all these features that, from the point of view of macroscopic equilibrium states, are related to the distribution of local bonds, provided by the peripheral electrons of the substitute atoms dissolved in the Ni matrix.
Keywords: statistics of Ni-Ni bonds, Ni-based alloys and magnetic moments.

1. Introduction

The quantum character of metallic and covalent bonds between one Ni atom and its first order neighbors supports the band model adopted to explain the magnetic behavior of pure Ni, and of binary and ternary solid solutions of Ni with diamagnetic elements, and especially for the Ni-Cu systems. The linear drop of magnetization and of the Curie temperatures with the concentration of non-magnetic elements dissolved in a Ni matrix was initially analyzed by using the energy band model [1, 2]. Subsequent measurements showed that in the range of critical concentrations the model of neighbor dependent atomic moments, applied for Ni-Cu alloys, predicts that the magnetic moment remains the same as in pure metal [3, 4], if at least 8 of its 12 first order neighbors are Ni atoms. For binary alloys $Ni_{1-x}D_x$, the decrease in the magnetic moment depends not only on the concentration $\boldsymbol{x}$ of the non-magnetic element D, but also on the electronic structure of the substitute atoms. For Ni-multi component solid solutions, such as ternary solutions analyzed here, the decrease in the magnetic moment considers the average electronic concentration of the diamagnetic matrix [5-8].

2. Modeling Statistics

In the followings, a statistical theoretical model is proposed for the distribution of inter-atomic bindings between the nearest neighbors in Ni-based solid solutions. In a metallic crystal, the first order atoms are bonded by quantum interactions whose statistical character predicts a higher probability density of finding the extra-electrons among the first order neighboring atoms. From the quantum point of view, the spatial overlapping of the wave functions describing these electrons provides the prevalent metallic character of the inter-atomic bonds that determine the physical properties of the solid.

In the cases of Ni face centered cubic crystal, the distribution and strength of the 12 bonds with the nearest neighbors are the same in every equivalent position of the crystalline lattice. For solid substitutional solutions of Ni with other elements, some of the 12 bonds Ni-Ni with the first order neighbors may be substituted with $k = 0, 1,2,\ldots 11, 12$ Ni-D bonds, where D are any type of the nonmagnetic atoms that substitute the Ni atoms. From the crystallographic point of view, in pure Ni, all the 12 Ni-Ni bonds of each atom, are identical (Fig. 1-a). In solid substitutional solutions, a solute atom, having a different electronic structure, will affect in a different way the intensity and the number of these bindings (Fig. 1-b). This means that in Ni based solid solutions, the number of the affected bonds increases with the average concentration of the diamagnetic matrix electrons not only with those of diamagnetic atoms. In certain early studies [1, 2] on the solid binary solutions of Ni with Cu, Zn, Al, Si, this parameter are considered an integer equal to *1, 2, 3, 4*; i.e., and the dissolved elements are mono, bi, tri, and tetravalent species, respectively. In the studies [5-8] this parameter is considered as the average concentration of the electrons that are involved in the Ni-D bonds. Actually these non integer values are more accurately determined and shown to be rational, as they are diminished by a certain covalence degree in the "pure metallic" bonds, provided by the conduction band electrons. In multi-component alloys, the electronic concentration that may serve to analyze the drop in the magnetic moment is: $n = \sum_{i=1}^{p} n_i x_i$, *(1)*

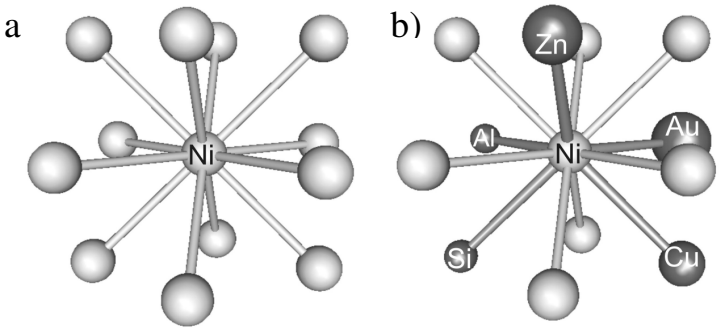

Fig. 1. Chemical bindings of one Ni atom with its 12 nearest neighbors, in a) pure nickel and b) substitutional solutions

where $p=i+1$ represents the number of non-magnetic components dissolved in the Ni matrix.

Weighted average concentration in ternary $Ni_{1-x-y}Cu_xD_y$ alloys, is $n = n_{Cu}\,x + n_D\,y$.

Further considerations on this electrically neutral crystalline system; reveal that every Ni atom is now involved not only in Ni-Ni bonds, but also in specific Ni-Cu and Ni-D bonds. Thus, each binary, ternary or multi-component Ni-based solid solution, where the average concentration of the diamagnetic matrix electrons is less than unit, $n \leq 1$, a hetero-system of the type $Ni_{1-n}D_n$ can be considered. In this the Ni-Ni bonds concentration drops with increasing number of Ni-D bindings, i.e., with the concentration of the extra-electrons of the hetero atoms dissolved in the Ni matrix. In the whole volume of a sample, the unaltered Ni-Ni bonds will have the concentration equal to *1-n*, and the Ni-D bindings will have a concentration *n*, equal to the electron concentration of the diamagnetic matrix. In such alloys, of a centered faces cubic internal symmetry (CFC), the probability that *k=0, 1, 2,..., 12* of the 12 possible bonds of one Ni atom, realized by the electrons of the different solute non-magnetic atoms, is the combined probability:

$$p_n(k) = n^k\,(1\text{-}n)^{12\text{-}k}\,. \qquad (2)$$

The positioning in one of the 12 equivalent sites of all equivalent bonds of the Ni atoms with its first order neighbors, may take place in a number of ways given by:

$$C_{12}^{k} = \frac{12!}{k!(12-k)!}\,. \qquad (3)$$

The total probability or the concentration of Ni atoms that have *k b*onds with their first order foreign neighbors will thus be given by the equation:

$$P_{12}(k) = C_{12}^{k} n^k (1-n)^{12-k}\,. \qquad (4)$$

By adding up the probabilities that correspond to different values of *k*, one obtains the binomial distribution function:

$$F_{12}(m,n) = \sum_{k=0}^{m} P_{12}(k) = \sum_{k=0}^{m} C_{12}^{k} n^k (1-n)^{12-k}\,. \qquad (5)$$

This represents the probability that a Ni atom is bonded to its 12 first neighbors by a maximum number *m* of bindings provided by the extra-electrons of the non-magnetic atoms dissolved in the Ni matrix.

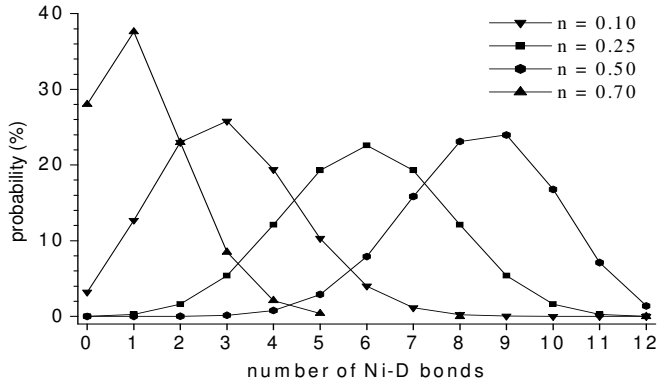

Fig. 2. Distribution of Ni atoms as a function of Ni–D bonds number for different average electron

The graphs in figure 2 presents the distribution of the Ni atoms versus the number of the *12-m* bonds between Ni-Ni, or else, the statistical distribution of the Ni atoms connected with their

first order atoms via the peripheral electrons of the non-magnetic atoms of Ni based alloys. One can realized that the each distribution versus Ni-D bonds number will be symmetrical with the corresponding distribution of Ni-Ni bonds number.

In figure 3, the family of curves given by *m = 0, 1, 2,…, 11*, show how the number of Ni-Ni bonds decreases with increasing the conduction electrons concentration, for the hetero atoms dissolved in the Ni matrix. One observes that, for a unit concentration *n=1*, of the extra electrons of diamagnetic atoms dissolved in Ni, all the Ni-Ni bonds are affected.

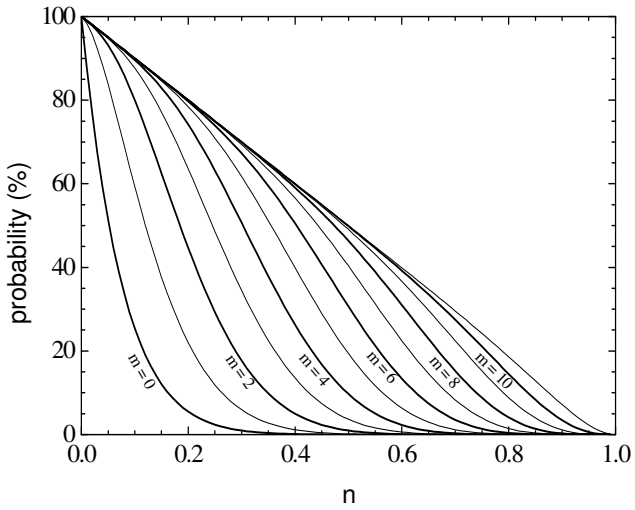

Fig.3. Drop in the probability of maximum number *m = 0, 1, 2,..., 11 of* Ni-Ni bonds in the Ni_{1-n} D_n system

3. Results and discussions

Figure 4, presenting a graph based on our original experimental data [5-7], show that the magnetization follows the same thermo dependency for ternary alloys with diverse atomic Ni concentrations, having quasi-identical electronic concentration of the diamagnetic matrix. The mean concentration has been calculate taking $n_{cu=}1$, $n_{Zn}=2.1$ $n_{Al}=2.9$ $n_{Si}=3.4$ $n_{Au}=0.7$. This supports the hypothesis that the average concentration of peripheral electrons located in valence shell of the dissolved atoms in the Ni matrix, determine the distribution of these atoms connections with their first order neighbors, or else, of the short distance interactions that determine the ferromagnetic order.

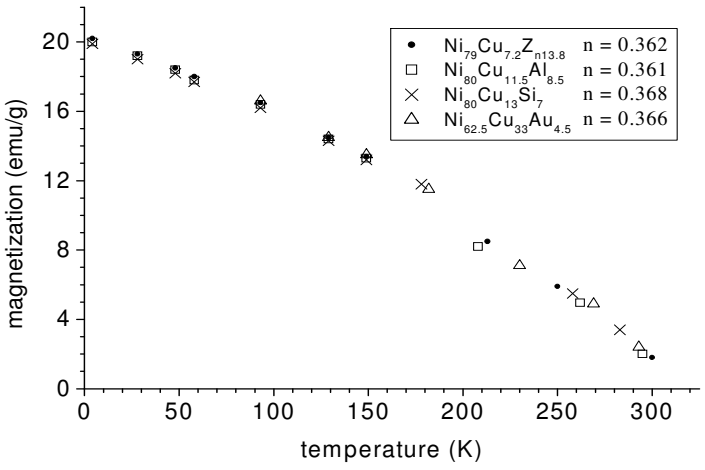

Fig. 4. Magnetization versus temperature for $Ni_{1-n}D_n$ heteroalloys

The graph shown in figure 5 even better supports the fact that the average magnetic moment has the same value for identical electronic concentration of the diamagnetic matrix, regardless the fact that the Ni atoms concentrations are different. One can see a shift from the linear decrease of the magnetic moment for electronic concentrations *n>0.5*.

The continuous line represents the graph of the theoretical dependency of the magnetic moment, calculated as a statistical average value, given by the equation:

$$\mu(n) = \mu_{Ni}(1-n)\sum_{k=0}^{4} C_{12}^{k} n^{k}(1-n)^{12-k} = \mu_{Ni}(1-n)P_4(n)\,. \qquad (6)$$

This best describes the experimental results, especially in the range of critical concentrations.

In this model of bonds dependent magnetic moments, $P_4(n)$ represents the probability to find a Ni atom bonded through less than 5 (i.e. 1-4) connections due to the extra-electrons of non-magnetic atoms dissolved in the Ni matrix. Since $P_4(n) = P_8(1-n)$, one can say that only those Ni atoms will remain under ferromagnetic order, that are linked via more than 8 (i.e. 9-12) Ni-Ni bonds.

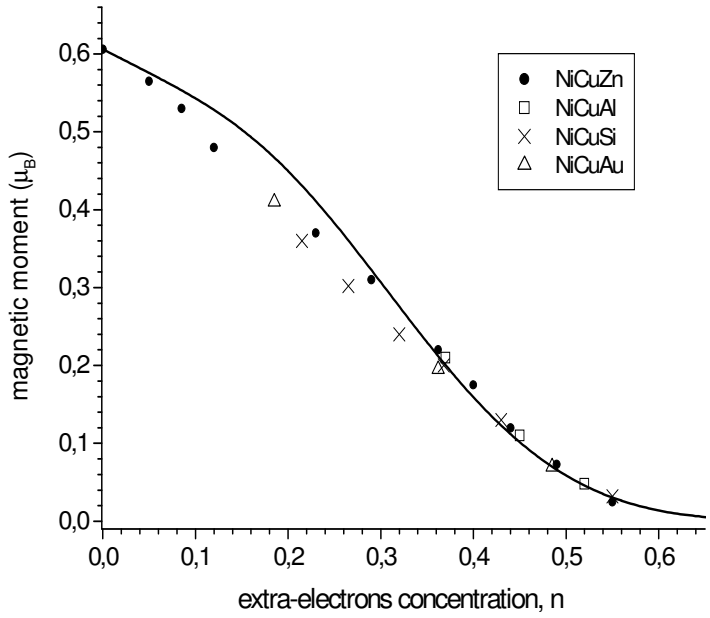

Fig. 5. Magnetic moment versus electrons concentration *n:* experimental and theoretical graph

4. Conclusions

The magnetic behavior of Ni-based alloys may thus be discussed within the statistics of the nearest neighbor's interatomic bonds. Based on certain experimental results reported in literature [3, 4], one assumes that in Ni-Cu alloys, only those Ni atoms that have more than 8 nearest neighbors, also have a magnetic moment exactly equal to that of pure nickel. This model of the neighborhood dependency of the average magnetic moment is in a good agreement with experimental results and explains the shift from the linear drop of the

magnetization with increasing copper content, in the critical range of the ferromagnetic to paramagnetic transition. Even more accurate measurements show that even for other binary solid solutions of Ni with diamagnetic elements, diminishing of the average magnetic moment and the drop in the Curie temperature indicate non integer, rationale values of the slope, in a concentration dependent graph. These findings may be interpreted in the bands model, by the gradual filling of the Ni 3d band with conduction electrons of the non-magnetic atoms.

Starting from previous studies on solid ternary solutions $Ni_{1-x-y}Cu_xD_y$, where D is Zn, Si, Au or Al, in present study, we showed that the drop in the ferromagnetic interactions in Ni may be analyzed following a general approach, as a function of Ni-Ni non affected bounds by the extra-electrons of non-magnetic atoms dissolved in the Ni matrix. The above statistical considerations combined with the binomial distribution give, in the general case, the value of the mean magnetic moments of Ni-based solid solutions. Our probabilistic model shows that the disappearing of one Ni atom ferromagnetic moment can be assigned to the replacement of at least four Ni-Ni bonds out of twelve, existing in pure nickel bulk, with non originally Ni-Ni bindings

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