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1989 J. Phys.: Condens. Matter 1 7329

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Calculated magnetic behaviour for the $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ pseudo-binary alloys

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Received 13 March 1989

Abstract. Spin-polarised energy band calculations for the hexagonal pseudo-binary alloy system $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ are reported. The calculations were performed for seven different concentrations with an ordered structure ($x = 0, \frac{1}{6}, \frac{2}{6}, \frac{3}{6}, \frac{4}{6}, \frac{5}{6}$ and 1). Good agreement between experiment and theory was obtained for the magnetic moments. There are two non-equivalent positions in Fe_2P (Fe(I) and Fe(II)). From total-energy calculations, as well as from arguments based on the magnetic properties, we conclude that there is a preferential occupation of the Ni atoms on the Fe(II) site.

1. Introduction

Experimentally it is found that Fe_2P forms in a hexagonal structure with space group $\overline{\text{P}}6_2\text{m}$ (D_{3h}^2) [1]. The iron atoms occupy two inequivalent atomic positions and we will refer to them as the I and II sites, respectively (figure 1(a)). In the Wigner–Seitz cell there are three atomic positions of type I and equally many of type II. The I site (marked as an open circle in figure 1(b)) is surrounded by four phosphorous atoms which form a tetrahedron, while five phosphorous atoms form a pyramidal configuration around the II site (marked as a full circle in figure 1(b)). In the following we will use the notation $(\text{A}_n)(\text{B}_{6-n})\text{P}_3$ where the first and second parentheses stand for the occupation of site I and site II, respectively.

From polarised neutron diffraction studies on single crystals at 77 K it has been found that the magnetic moments in Fe_2P are ferromagnetically ordered and directed along the hexagonal c axis [2]. Their magnitudes are $0.92 \mu_{\text{B}}$ and $1.70 \mu_{\text{B}}$ for the I and II sites, respectively. Powder neutron diffraction measurements, also at 77 K, gave $0.96 \mu_{\text{B}}$ and $2.31 \mu_{\text{B}}$ for the I and II sites respectively [3]. Experimental data for the total magnetic moment are 2.92 – $2.94 \mu_{\text{B}}$ per formula unit [4]. On the theoretical side, energy band calculations have been reported. Here it was found that both the calculated total moment ($2.97 \mu_{\text{B}} \text{FU}^{-1}$ [5], $2.94 \mu_{\text{B}} \text{FU}^{-1}$ [6]) as well as the individual moments ($0.76 \mu_{\text{B}}$ [5], $0.96 \mu_{\text{B}}$ [6]) for the I site and ($2.31 \mu_{\text{B}}$ [5], $2.04 \mu_{\text{B}}$ [6]) for the II site agree with the experimental data. The fact that Fe_2P has very different iron moments on the two sites makes it a very interesting system to study.

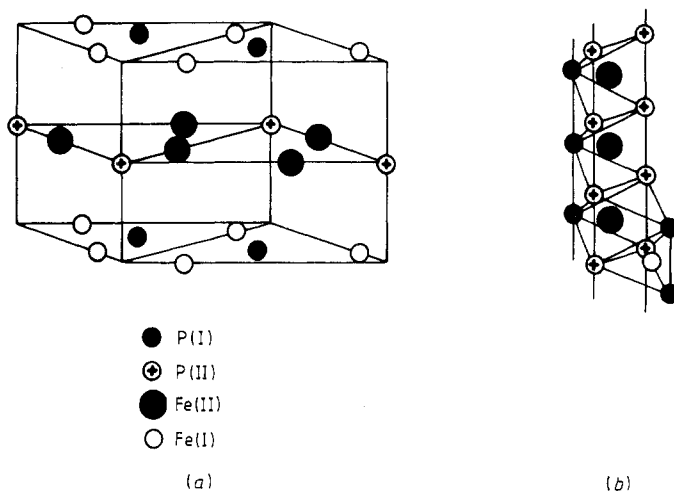


Figure 1. (a) Crystal structure of Fe₂P. The P(I) atom is denoted by a small full circle, the P(II) atom by a small circle with a cross, the Fe(I) atom by a small open circle and the Fe(II) atom by a large full circle. (b) Geometrical arrangement of the phosphorous atoms around the Fe(I) and Fe(II) atoms. The atom types are denoted in the same way as in (a).

Nickel shows complete solid solution in the hexagonal system (Fe_{1-x}Ni_x)₂P [7]. The crystal structure remains the same for all concentrations (the same as in Fe₂P, figure 1(a)). Experimentally it is found that when substituting Fe with Ni in the ferromagnetic compound Fe₂P, the total magnetic moment decreases. When the Ni concentration exceeds a certain critical value, the magnetic moment is lost and a temperature-independent paramagnetism is observed [7]. Since the Wigner-Seitz cell contains two different types of phosphorus atoms (one P(I) and two P(II)) and two different metal positions (three Fe(I) and three Fe(II)—see figure 1) it is of interest to study theoretically if any position is occupied preferentially by Fe or Ni. In connection with this it is also of interest to see to what extent a preferential occupation affects the individual site-decomposed magnetic moments. Furthermore it is interesting to see if a theoretical treatment can account for the loss of magnetism at high nickel concentrations in these alloys.

2. Details of the calculations

In order to study theoretically the influence of substituting Fe with Ni on the magnetic moments in the Fe₂P compounds, we have performed electronic structure calculations. This was done by simulating the electronic structure of the pseudo-binary alloy by that of an ordered compound with the same stoichiometry (similar approaches can be found in [8]). Since there are six different atomic positions that are occupied by either Fe or Ni, we can calculate the electronic structure for seven different concentrations, i.e. Fe₆P₃, Fe₅NiP₃, Fe₄Ni₂P₃, Fe₃Ni₃P₃, Fe₂Ni₄P₃, FeNi₅P₃ and Ni₆P₃. For the ternary compounds we can in addition vary the atomic distributions between site I and II.

The calculations were done using the linear muffin tin orbital (LMTO) method with the combined correction terms [9]. The density of states (DOS) was calculated using the analytical tetrahedron method [10]. We obtained final convergence by sampling the

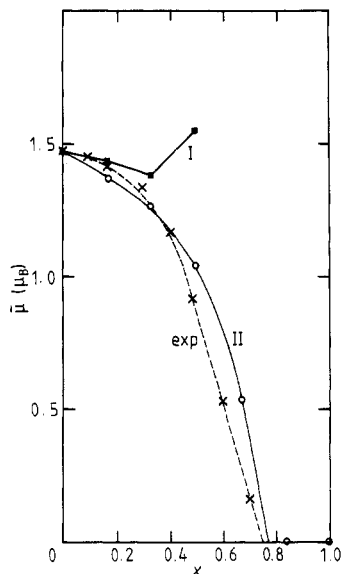


Figure 2. Total magnetic moment per Wigner-Seitz cell divided by the number of Fe atoms in the cell. The curve denoted by 'exp' refers to the experimental data ([7]). The curve marked I refers to the theoretical calculation when we put the Ni atoms onto the I site preferentially, whereas the curve marked II refers to when the Ni atoms are put onto the II site.

irreducible part of the Brillouin zone (BZ) at 45 k -points. In the generation of a self-consistent charge density the core electrons were kept frozen. Furthermore the local spin density approximation was used with the von Barth–Hedin parameterisation of the exchange and correlation potential [11]. The crystal structure was the same for all concentrations, i.e. the crystal structure of Fe_2P . This hexagonal compound has a c/a ratio of 0.5848. For further details concerning the computational aspects and the crystal structure see [6].

3. Results

When the Ni atoms replace the Fe atoms in Fe_2P , forming the $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ alloy, they can occupy either the I site or the II site (figure 1). In our calculations we can account for this by simply putting the Ni atoms onto a specific site. In figure 2 we show the average magnetic moment per Fe atom for the $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ system with three curves; one refers to the experimental data [7] and the other two to theoretical values where we have put the Ni atoms preferentially into the I or II positions, respectively. Here we notice that the experimental curve is well reproduced by the theoretical curve with the Ni atoms being put into the II position. In contrast we find that the curve that refers to the Ni atoms in the I position deviates considerably from the experimental data for larger Ni concentrations. In figure 3 we show the individual Fe and Ni moments obtained from the calculations. Again we distinguish between the two cases where we have put the Ni atoms preferentially onto the I or II sites and the calculated curves have been labelled accordingly. First of all we notice that for all Ni concentrations, the Fe atoms carry a much larger magnetic moment than Ni. In accordance with previous calculations for Fe_2P [5, 6] we find in this work that, for all concentrations, the moment at the II site is much larger than the moment at the I site. We also see that when we put the Ni atoms onto the I site, the partial Fe moments of the other I sites as well as the II sites drop faster with increasing Ni concentration than when we put the Ni atoms into the II site.

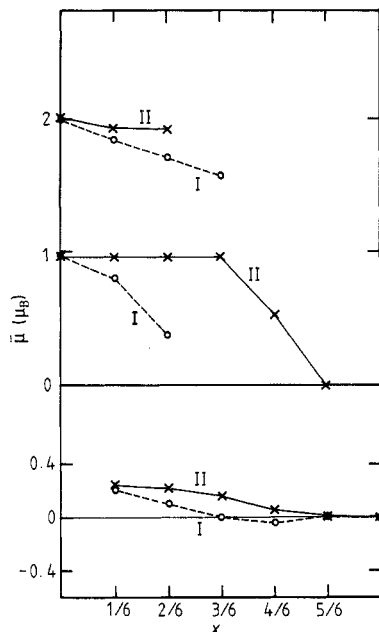


Figure 3. Atomic-site projected magnetic moments for $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ ($x = 0, \frac{1}{6}, \frac{2}{6}, \frac{3}{6}, \frac{4}{6}, \frac{5}{6}$ and 1). The upper panel shows the Fe partial moments and the lower the Ni moments. The curves marked I refer to the calculation where we put the Ni atoms into the I site preferentially, whereas the curves marked II refer to when the II site is substituted.

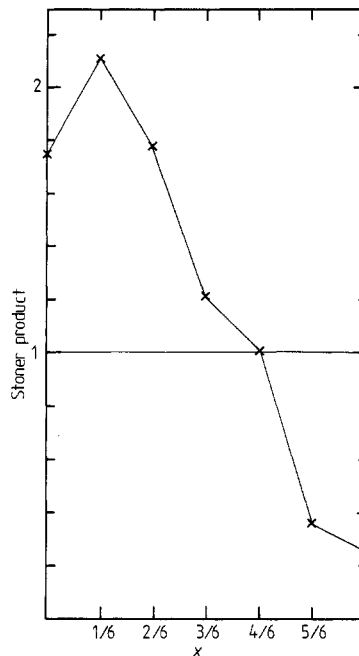


Figure 4. Stoner product for the $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ systems ($x = 0, \frac{1}{6}, \frac{2}{6}, \frac{3}{6}, \frac{4}{6}, \frac{5}{6}$ and 1).

In fact putting the Ni atoms into the II position results in a remarkably stable situation where the individual Fe moments at both sites I and II seem to be almost unaffected by the influence of the Ni atoms in the nearest-neighbour positions. The decrease in the average magnetic moment with increasing Ni concentration (figure 2) for this situation then comes about because we replace an Fe atom, with a magnetic moment of about $2\mu_B$, with a Ni atom which carries almost no moment.

In view of the calculated as well as measured dependence of the average magnetic moment on the Ni concentration, it is interesting to compare with other pseudo-binary magnetic systems. In many pseudo-binary magnetic systems that contain Fe together with substituted Co or Ni atoms, there is a clear trend in the behaviour of the magnetism. On the iron-rich side of the pseudo-binary alloy there is often an increase in the magnetic moments when Fe is substituted by Co or Ni. At a certain concentration of substituted Co or Ni atoms, the magnetism reaches a maximum before it decreases (see, for example, [12]). This effect has been explained as a filling of a strongly hybridised majority spin band when Co or Ni substitutes for Fe. When the majority spin band is filled this forces the added valence electrons, connected to the Fe substitution, to populate the strongly hybridising minority spin band. Consequently there will be a maximum before the magnetic moment decreases. This behaviour is often referred to as a Slater–Pauling

curve. Figure 2 obviously does not show such a maximum in the magnetic moment when we substitute Fe with Ni. One could possibly view the curve in figure 2 as being on the right-hand side of a Slater–Pauling curve, i.e. saturation is already reached in Fe_2P . Normally, however, one finds that it is for an average population of the 3d band exceeding the number of 3d electrons in Fe that corresponds to the maximum in the Slater–Pauling curve. Therefore, if the curve in figure 2 were described as a Slater–Pauling curve, one would calculate an anomalously large number of 3d electrons residing on the Fe atoms in Fe_2P . This is not what we find, since the number of Fe 3d electrons takes the normal value of about 6.7 per Fe atom for all compounds in the above calculations. Hence we must conclude that figure 2 is *not* a Slater–Pauling curve. Instead, as mentioned above, the behaviour of the average magnetic moment is connected with the fact that the Fe and Ni atoms seem to carry fixed moments irrespective of the local environment (which is the case for the II substitution). Therefore substituting an atom with a high-spin moment (Fe) by an atom with a low-spin moment (Ni) reduces the total magnetic moment.

Since we get agreement with the experimental moments only when we put the Ni atoms into the II site, we can argue that Ni substitutes Fe preferentially at the II position [7]. Figure 2 shows that experimentally the magnetic moment has disappeared when the Ni concentration is larger than about 70%. If we extrapolate our theoretical results to a zero magnetic moment we get a critical concentration of about 77%, which compares fairly well with experiment [7]. In order to investigate the onset of ferromagnetism we show in figure 4 the calculated Stoner product for all Ni concentrations. This figure refers to the calculation where we artificially substitute Fe with Ni on the II site. Here we see that the magnetic moment disappears at a critical Ni concentration of 68%. This compares favourably with the experimental value and gives further support to the picture of Ni substituting Fe in the II positions preferably.

Another way to investigate the possibility of a preferential substitution is to compare the total energies for two cases with the Ni atoms in the I or in the II position, respectively. For instance we have calculated the total energy for the compound $(\text{Fe}_3)(\text{Ni}_3)\text{P}_3$ and compared it with the energy of the compound $(\text{Ni}_3)(\text{Fe}_3)\text{P}_3$. The notation here is that the atomic element listed first in the chemical formula is positioned at the I site (figure 1). For all studied cases we find that the energy is lowest when the Ni atoms occupy the II site. The energy is thus lower with 10 mRyd FU^{-1} when the Ni atom occupies the II site for the compound $(\text{Fe}_5)(\text{Ni})\text{P}_3$ compared to $(\text{Ni})(\text{Fe}_5)\text{P}_3$. For $(\text{Fe}_4)(\text{Ni}_2)\text{P}_3$ compared to $(\text{Ni}_2)(\text{Fe}_4)\text{P}_3$ the energy difference is 26 mRyd FU^{-1} and finally for $(\text{Fe}_3)(\text{Ni}_3)\text{P}_3$ it is 43 mRyd FU^{-1} . The energy gain in occupying the II position is thus larger than in occupying the I position and is consistent with our conclusion of preferential occupation, based upon the magnetic data. This picture is also consistent with our calculation of the electronic pressure. Since the atomic arrangement with the lowest total energy also corresponds to a situation with maximised chemical bonding we use the electronic pressure to investigate which atomic site is preferred. This is done by studying which atomic arrangement gives the most stabilising electronic pressure. For all investigated Ni concentrations ($x = \frac{1}{3}$, $\frac{2}{3}$ and $\frac{3}{3}$) we find that the electronic pressure is optimised when the Ni atoms occupy the II site preferably.

Experimentally it has been concluded that the Ni atoms do indeed populate the II position when the Ni concentration is larger than 30%. For lower Ni concentrations it was found that site I was preferred [7]. Hence it is only for larger Ni concentrations that theory agrees with experiment. However the trend of the energy gain in occupying the II site is given correctly by our calculations since the energy gain increases with Ni

concentration, although it seems that our theoretical treatment somewhat overestimates the tendency for Ni to occupy the II site.

4. Conclusions

From our theoretical calculations we find that Ni prefers the II site when it substitutes Fe. However there is experimental evidence that the Ni atoms prefer the I site at lower Ni concentrations. This disagreement between experiment and our theoretical results might emanate from the spurious long-range order of the calculations. The spurious long-range order does not, however, appear to be crucial for the description of the magnetic moments, since we can account for both the critical concentration for the disappearance of magnetism as well as the absolute values of the magnetic moments. There is also previously published work where the spurious long-range order seems to have relatively little influence on the magnetic properties [8]. The experimental data for the magnetic moments also support the theory that the Ni atoms occupy the II site, since only when we put the Ni atoms into this site do we reproduce the measured moments for larger Ni concentrations. Finally it should also be mentioned that the experimental situation might be somewhat unclear, the data showing some dependence on the sample preparation. Depending on the technique of annealing the sample, different behaviour regarding the site preference of the substituting Ni atoms was observed [7].

Acknowledgments

O Eriksson is grateful to The Bank of Sweden Tercentenary Foundation and B Johansson and B Noläng are grateful to the Swedish Natural Science Research Council for financial support. Valuable discussions with S Rundqvist are acknowledged.

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