Site/preferences and local spin-polarization of transition metal solute atoms in B2 type Ni–Al alloys

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ABSTRACT

In the framework of the Local Spin Density Approximation we study the electronic structure, site preference energies and magnetism in B2 Ni50(Al37.5Ni12.5) alloys doped with 3d-transition metals using a Coherent Potential Approximation for treating effects of substitutional disorder. We find that the lattice expands also for non-magnetic Ti and V substitutions and thus this effect cannot entirely be related to magnetism as it was conjectured earlier. Except Co all TM atoms are found to prefer the Al sublattice. For the magnetic substitutions (Cr, Fe, Mn) we also find that the lattice expands independently on the state of magnetic order – only local atomic spin-polarization is important. An effective magnetic coupling between substituted atoms has been calculated and it is shown that it does not scale with the magnitude of the local moments.

1. Introduction

Ni–Al alloys with B2 structure attract a considerable interest since their technological importance because of their outstanding chemical and mechanical properties [1]. Theoretically, on the ab-initio level, the electronic structure and also various other properties, like defect formation energies, of these alloys have been intensively investigated (see Ref. [2] and references therein). There exists also a couple of theoretical studies on the effects of transition metal alloying to B2 Ni–Al alloys [3]. Such alloying has been found to improve the ductility of the alloys (see e.g. Ref. [4]) and also in some cases leads to an unusual softening behavior [5,6].

The latter effect has been thoroughly studied by Fu et al. [7], who, using a combination of experiments and first-principle calculations, have argued that the magnetism of the transition metal solute atoms plays an important role. It has been shown that the softening caused by Fe, Mn and Cr substitutions in Ni–40Al alloy and the site preferences are magnetically driven, i.e. being a result of the spin-polarization of the solute atoms on the Al sublattice. It was found that Co atoms prefer the Ni lattice sites and are non-magnetic so that their substitution has no effect on the lattice parameters and hardening behavior [7] (see also review [8]). Very recently the magnetism in these ternary alloys has been studied using Mössbauer spectroscopy [9] and neutron diffraction [10] techniques where it has been found that Co occupies almost equally the Ni and Al sites. Although the proposed scenario [7,8] explains the hardening behavior in case of Fe and Co substitutions the situation concerning Cr and Mn substitutions, which are magnetic, prefer Al sites, but lead to the less pronounce or even vanishing softening, remains unclear. One should also note that the calculated Mn moment in an Ni–Al host is much larger than that of Fe and that the Mn substitution has more pronounced impact on the lattice constant than that of Fe.

In the work presented here we have performed a first-principle study of structural and magnetic properties of B2 Ni–Al–TM alloys (TM = transition metal). Compared to the previous study, which has been based on the super-cell approach [7] we have used the conventional Coherent Potential Approximation (CPA) for treating the effects of atomic substitutional disorder in these alloys. A study similar to our CPA calculations for transition metal substitutions in Ni3Al super-alloys with L12 ordering has been reported earlier [11]. To be consistent with previous calculations [7,8] we have chosen the Ni50(Ni12.5Al37.5) alloy as a reference for studying the effects of TM substitutions, but extend the investigation to the whole 3d series (Ti–Cu). We have found a couple of interesting and unexpected results: Although Ti and V are non-magnetic they strongly prefer Al sites and lead to a much larger lattice expansion in comparison to the magnetic substitutes Mn and Fe. In our calculation Co atoms show almost no site preferences thus explaining recent neutron diffraction results. In addition we have calculated the effective exchange interactions between the magnetic solute atoms, which are found not to scale with the size of the solute...
moments. Employing the Disordered Local Moment (DLM) technique we also investigate and discuss the influence of magnetic disorder effects on the lattice constant, which allowed us to rule out the influence of the induced polarization of the Ni host on the softening behavior. It is found that the consideration of a more realistic state than just ferromagnetic order for the description of a magnetic state these alloys does not change our conclusions about the role of the atomic spin-polarization on the lattice constant. It thus appears that the hypothesis [7] concerning the role of the lattice expansion on the hardening in these alloys is consistent with our new results.

2. Method of the calculation

To investigate the electronic structure, site preferences and influence of transition metal (TM) substitutions on the lattice constant and the magnetism of Ni_{62.5-x}TM_{x}Al_{25} alloys we employ the scalar relativistic Korringa–Kohn–Rostoker (KKR) method in combination with the atomic-sphere approximation (ASA) as described in Refs. [12,13]. The calculations are done in the framework of the Local Spin Density Approximation (LSDA) including the General Gradient Approximation (GGA) parameterizations by Perdew, Burke and Ernzerhof (PBE) [14] for the exchange and correlation potential. The spherical harmonic expansion of the charge density within an ASA sphere was considered up to l = 6. We have also taken into account multipole moment contributions to the electrostatic energy as described by Ruban et al. [15]. The summation over multipole moments for the electrostatic part of the one-electron potential and the total energy is carried out up to \( l_{\text{max}} = 6 \). With these corrections [15] the description of the total energy becomes comparable to calculations using a full charge density. A uniform mesh of \( 25 \times 25 \times 25 \) k-points has been used for performing the integration over the Brillouin zone.

The effects of chemical disorder on one or both sublattices of the B2 structure were taken into the account in the framework of the single site Coherent Potential Approximations (CPAs) [16]. The size of ASA spheres was chosen to be equal on both sites of B2 lattice. The CPA total energies of \( \text{Ni}_{50-x}\text{TM}_{x}(\text{Al}_{37.5}\text{Ni}_{12.5}) \) and the corresponding equiatomic \( \text{Ni}_{50}(\text{Al}_{37.5}\text{Ni}_{12.5}) \) alloys have been compared after lattice constant optimization to calculate the site preference energies of the TM atoms substituted for Ni. In order to simulate the paramagnetic state with local atomic moments, which can be expected in the alloys doped with Mn and Cr, we used the Disordered Local Moment (DLM) formalism as embodied in the KKR method as described and discussed in detail by Gyorffy et al. [17]. In the DLM formalism the paramagnetic disorder is modeled by considering a pseudo-alloy with randomly distributed magnetic atoms with spin-up and spin-down and applying the standard CPA. In the present case of Ni–Al–TM alloys, this is achieved by splitting the alloy into “spin-up” and “spin-down” atoms which are treated like 2 component of an ordinary alloy e.g. TM{spin-up}_{\alpha}/2 TM{spin-down}_{\alpha}/2.

3. Site preferences and role of the spin-polarization

In Fig. 1 we show the calculated energy differences between \( \text{Ni}_{50-x}\text{TM}_{x}(\text{Al}_{37.5}\text{Ni}_{12.5}) \) and \( \text{Ni}_{50}(\text{Al}_{37.5}\text{Ni}_{12.5-x}\text{TM}_{x}) \) alloys for three different concentrations of a TM solute (energies are given per unit cell of the B2 structure). All the transition metal substitutions but Co prefer to replace Ni on the Al sublattice rather than on the Ni one. However, the energy difference for Co is so small that this in fact would lead to an almost random distribution of Co atoms on the B2 lattice, which is in full agreement with recent experiments, which indicates only “slight” [10] site preference for Co atoms [3,10]. It is also interesting to note that this weak Co site preference found in Ref. [3] and Ref. [10] is different indicating, in particular, that relevant energy differences are indeed very small. These results for Cr, Mn, Fe and Co substitutions are also in agreement with the 32 atom super-cell calculations in Ref. [7]. However, since in our calculations we ignore lattice relaxations (because of the use of the atomic-sphere approximation) the prediction of Ni site preferences for Co should be taken with care. This is due to the fact that the small energy difference is the order of magnitude of the relaxation energies in random substitutional alloys: 0–0.2 eV per solute atom [18,19]. For all other transition metal solutes presented in Fig. 1 the relevant energies are almost an order of magnitude larger so that omitting local relaxations are not crucial.

We also find that Cr–Co atoms have magnetic moments if they are on Al sites whereas stay non-spin-polarized being on Ni positions. However, our calculations for non-magnetic substitutions for elements on the both edges of the 3d series Ti, V and Cu also show a strong preference for Al positions. We thus can rule out any important role of magnetism on the site preference tendencies contrary to earlier conjectures [7]. The site preference energies (Fig. 1) show a clear trend across the series having a minimum at Co and growing monotonically approaching the edges of the series. This trend is therefore related to some features in the p–d hybridization mechanism rather than to magnetic properties of solute atoms.

4. Lattice constant changes due to alloying and magnetism

Now we turn to the question how the solute atoms influence the lattice constant. As it was advocated in Refs. [5,7] the understanding of this issue may be a key for the explanation of hardening effects caused by alloying of a third element (see also the Introduction). Here, however, we restrict ourselves to the discussion of the role of the spin-polarization on the lattice constant changes. In Fig. 2 we plot the calculated lattice constant for \( \text{Ni}_{50}(\text{Al}_{37.5}\text{Ni}_{12.5-x}\text{TM}_{x}) \) alloys, which is lowest in energy (except for a Co solute). We also plot the corresponding values for pure Ni–Al alloys for comparison, where formally Al replaces Ni. In agreement with super-cell studies and experimental observations [8] Fe substitution for Ni leads to an essential increase of the lattice constant, whereas Co substitution does not. One can also see that Mn or Cr substitutions lead to an increase in the lattice constant, which is larger than for Al only. This is not the case if Fe, Mn, and Cr replace Ni on the Ni sublattice (Fig. 3) where they are non-magnetic. In this respect our CPA results are in agreement with Refs. [7,8]. We
also find that non-magnetic substitutions – Ti, V and Cu also lead to an increase in the lattice constant. Unfortunately no experimental information about these cases is available.

A standard spin-polarized calculation presented here and in Refs. [7,8] assumed ferromagnetic order of the magnetic solute atoms. The calculated moments of Fe, Mn, and Cr on Al sites are essentially larger than the corresponding moments of the pure metals. Moreover, there is also an induced spin-polarization on the Ni sites. Such magnetic interaction between solute atoms and host has been proposed to be one of the mechanisms leading to the hardening and the lattice expansion [8]. However, due to the low concentration of the magnetic solute atoms the alloys considered are paramagnetic down to very low temperatures [8]. The magnetic moments of the solute atoms are essentially in a thermally disordered state in all cases of physical interest so that the spin-polarization of the host Ni and Al essentially vanishes. In order to check how the magnetic disorder alters the calculated lattice constant, we perform calculations using a disordered local moment approximation where the magnetic atoms with spin-up and spin-down are equally distributed over the sublattice resulting in a total magnetization equal to zero [17]. The results for Mn and Cr are shown in Fig. 4 and clearly demonstrate that, although the host polarization vanishes, the lattice constants remain almost unchanged. This observation leads to the important conclusion that the host spin-polarization should be ruled out as possible mechanism for hardening caused by a magnetic solute and only the formation of the local magnetic moments on Cr, Mn and Fe may be relevant.

5. Magnetic interactions between solute atoms

Finally in Fig. 5 we show the calculated magnetic moments per solute atoms, including the host polarization, in Ni_{50}(Al_{37.5}TM_{12.5}) alloys. It can be seen that the magnetic moment reaches its maximum value in the middle of the 3d series (Mn), and decreases if we move toward the edges of the series as it was also found for the full potential super-cell calculations [7]. Since it is known that the elements from the middle of 3d series (Cr, Mn) usually order antiferromagnetically, we were motivated to study the effective exchange interactions by calculating $J_0$ (shown in Fig. 5) to reveal the character of interactions in Ni_{50}(Al_{37.5}TM_{12.5}). The $J_0$ parameter is defined as the sum over all Heisenberg pair exchange constants $J_0 = \sum_{i,j} J_{ij}$ taken for a given magnetic atom, where $J_{ij}$ are the parameters of the effective magnetic Hamiltonian $H = \sum_{ij} J_{ij} \vec{e}_i \cdot \vec{e}_j$, $\vec{e}_i$ are the directional units vectors for the magnetic moment on site $i$. The method of the calculation of $J_0$ has been devised by Liechtenstein et al. [20] as described in Ref. [21].
including the implementation in the KKR–ASA framework. A positive sign of $J_0$ means ferromagnetic character of exchange owing to the usual definition of the Heisenberg hamiltonian.

It turns out that the magnetic interactions are ferromagnetic for all TM solutes (Fig. 5). However, the size of the effective exchange does not scale with the value of the atomic magnetic moments. The effective interaction between Mn moments, which have the largest moments, is indeed smallest across the magnetic TM solutes whereas interaction between Co is largest despite the smallest moment. This suggests that in the case of Mn one might have a competition between distant antiferromagnetic couplings and nearest neighbor ferromagnetic ones. Although the largest value of the effective exchange is found for the Co case, one cannot expect a faster onset of the magnetic order in Co doped alloys than in Fe ones since the Co atoms have almost vanishing site preferences and thus are randomly distributed among Ni and Al sublattices. This means that a large portion of the Co atoms would be non-magnetic. Indeed, it has been found experimentally that Ni$_{50}$(Al$_{40}$Fe$_9$Ni$_1$) is magnetically ordered at low temperature [8] but no such reports exist for Co doped alloys.

6. Conclusions

We have shown that the interactions between magnetic TM solute atoms in Ni–Al alloys are essentially ferromagnetic. The moments formed on Cr, Mn, Fe atoms on the Al sublattice are localized, which follows from their robustness upon varying magnetic orders, i.e. keeping the same value of the local moments in FM and in DLM state. The spin-polarization of the Ni–Al host does not affect the lattice constants and can be ruled out as one of the mechanisms responsible for the observed softening behavior in these alloys. The formation of the local magnetic moments on the solute, greatly affects the d–d and d–p hybridization mechanism thus influencing the softening as has been proposed earlier [7]. The revealed mismatch between the dependence of the effective interaction and the values of the moment as well as the ferromagnetic character of the exchange for all TM magnetic solutes may, in our opinion, deserve further experimental attention.

Reference