Magnetic state, magnetovolume effects, and atomic order in $Fe_{65}Ni_{35}$ Invar alloy: A first principles study

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We employ the locally self-consistent Green's function technique and exact muffin-tin orbital method to investigate magnetic state and ground state properties of Invar $Fe_{65}Ni_{35}$ alloy. We show that it is in a chemically disordered state, characterized by a relatively small amount of atomic short-range order, above the magnetic ordering temperature. We speculate that it should remain in this state below the Curie temperature upon applying usual heat treatment for the Invar alloys. The magnetic state at the experimental lattice spacing is shown to be sensitive to the type of approximation for the exchange-correlation functional: While the magnetic ground state is purely ferromagnetic in the generalized gradient approximation, there is a small amount of Fe atoms with magnetic moment antiferromagnetically aligned relative to the global magnetization in the local density approximations. The local spin-density approximation, however, fails to yield correctly the equilibrium lattice spacing, whereas the generalized gradient approximation reproduces it reasonably well. The anomalous spontaneous volume magnetostriction leading to the Invar effect is found to be $\approx 3\%$, in fair agreement with the experimental estimate of $\approx 2.2\%$.

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I. INTRODUCTION

The anomalously low thermal expansion (Invar effect), discovered in fcc Fe-Ni alloys in 1897 by Guillaume,[1] is one of the oldest solid state physics phenomena, which still has not got a commonly accepted explanation. Similar thermal expansion (Invar-type) anomalies have been found thereafter in other metallic systems (see Refs. 2 and 3 for review), which showed that the Invar effect is a more common phenomenon, not specifically connected to the underlying crystal structure or chemical order. For instance, the Invar effect has been found in ordered alloys (Fe_3Pt, known as Invar2) and also in bcc Fe-Co alloys.[4] Moreover, the existence of an Invar anomaly in pure hcp Gd (Ref. 5) shows that this phenomenon is not entirely related to the transition metal magnetism.

However, for a long time the theoretical efforts aiming to explain the Invar effect have mainly been concentrated on Fe-Ni alloys, which are the oldest known, technologically most important and experimentally best investigated Invar materials. The most widely known picture of the Invar phenomenon in Fe-Ni was proposed by Weiss,[6] who suggested that the low thermal expansion originated from a thermal depopulation of high moment states with a larger volume and the corresponding filling of low moment (LM) states with a smaller volume. This theory, by assuming an existence of such two separated energy state (2γ-state model) and being further generalized, has provided a phenomenological background for the interpretation of the rather complicated physics found in fcc Fe based alloys.[7]

Despite the fact that high and/or low volume excitations have never been observed experimentally, the 2γ-state model of the Invar has been boosted two decades ago by first principles calculations performed for ordered Fe_3Ni (Ref. 8) and Fe_3Pt (Ref. 9) alloys. In these calculations, based on the local spin-density approximations (LSDAs), the energy of the ferromagnetic state was calculated as a function of the volume and the unit cell moment using a fixed spin moment (FSM) constraint. The total energy was found to have two separate minima at different volumes. The same minima were found later also in *ab initio* coherent potential approximation (CPA) calculations of disordered fcc Fe-Ni (Ref. 10) and Fe-Pt (Ref. 11) alloys. However, it has recently been shown that the appearance of two separated energy minima in Fe-Ni (Ref. 12) and Fe-Pt (Refs. 13 and 14) alloys at 0 K is the result of the collinear ferromagnetic constraint applied in these calculations, and would disappear if one allows for more general magnetic configurations.

Utilizing the results of the FSM calculations for ordered magnetic configurations of Fe_3Ni,[15–18] a microscopic model of the Invar effect was formulated, which went beyond the original simple 2γ-state model. In their work, it was pointed out[16] that the existence of two separated energy minima is indeed not crucial for the Invar effect to occur. The other important feature of these works is the use of the Ginzburg-Landau functional for a description of the long-wave limit of spin-fluctuation theory. The parameters of the functional have been determined from the total energy ferromagnetic FSM calculations of Fe-Ni alloys. Schröter *et al.*[17] have applied this model for random Fe-Ni alloys. However, the long-wave limit adopted in this work poorly describes the finite temperature magnetism of these alloys because of the localized nature of magnetic moments on Fe atoms. Besides, all the calculations have been done in the LSDA, which significantly underestimates the equilibrium volume.

The absence of the LM states has been recently established in a combined experimental and first principles theoretical investigation of Fe-Ni alloys.[19] In this work, the correlation between Mössbauer isomer shift and local magnetic moment has been established in the linear-muffin-tin orbital

(LMTO)-CPA calculations, and then it has been experimentally shown that the isomer shift for $Fe_{65}Ni_{35}$ Invar alloy is moderately decreasing with the temperature. The authors of this investigation concluded that the origin of the Invar effect is the nature of its *unusual* ferromagnetic state, with large, positive, and mostly frustrated exchange interactions.

It should be noted that although Fe-Ni Invar alloys are ferromagnets, there exists some experimental evidence that the zero-temperature ferromagnetic state in Fe-Ni Invar alloys is not homogeneous: It consists of some amount of atoms whose magnetic moments are either noncollinear or antiferromagnetically aligned.[20–29] Kondorsky and Sedov[30] were the first who proposed the "latent antiferromagnetism" or "mixed exchange" model for the magnetic state of Fe-Ni Invar alloys, which has been used to describe some experimentally observed properties.[26] The weak point of all these models is, however, the fact that all of them are purely phenomenological in the sense that they are not supported by first principles, i.e., parameter-free calculations.

The first *ab initio* noncollinear calculations of $Fe_{65}Ni_{35}$ were performed by Wang *et al.*,[31] who used the noncollinear version of the locally self-consistent multiple scattering method to calculate the distribution of the magnetic moments in a 256-atom supercell with sites randomly occupied by Fe and Ni. They have found that although the ground state was predominantly ferromagnetic, there were noncollinear configurations associated with Fe-rich regions. In particular, Fe sites surrounded completely by other Fe atoms had antiferromagnetic alignments, and Fe sites having less than three Ni nearest neighbors show noncollinear alignments.

This picture was consistent with earlier phenomenological models, predicting the coexistence of antiferromagnetism and ferromagnetism at low temperature. Later, van Schilfgaarde *et al.*[12] reported supercell calculations, which suggested that in Fe-Ni Invar at 0 K there is a continuous manifold of noncollinear spin configurations having a lower total energy than the collinear ferromagnetic one. The theoretical prediction of a noncollinear ground state[12] in Fe-Ni Invar has stimulated a substantial amount of experimental work in recent years,[32–35] which, however, did not find any kind of noncollinear magnetic states, except usual thermal spin-wave excitations.

The main reason for this disagreement is the fact that the equilibrium lattice constant in the calculations by van Schilfgaarde *et al.*[12] is much smaller (by 4%–5%) than the corresponding experimental value. This is an effect of the LSDA, which strongly underestimates the equilibrium volume of 3*d* metals and alloys (see, for instance, Refs. 36–38). This shortcoming also concerns the calculations by Wang *et al.*,[31] which were done for a lattice spacing of 3.49 Å, corresponding to the equilibrium LSDA volume for the $Fe_{65}Ni_{35}$ alloy. At the same time, a recently found peculiar behavior of Fe-Ni and Fe-Pt alloys under high pressure[39,40] indicates that the ferromagnetic state in these alloys indeed becomes unstable with respect to other magnetic states, presumably spin-glass-like, at smaller lattice spacings just before the transition to the paramagnetic ground state at higher pressure.

The physical origin of noncollinear states in Fe-Ni Invar alloys at small volumes was explained in a recent paper by Ruban *et al.*,[41] who showed by direct calculations of the exchange interaction parameters that the Fe-Fe antiferromagnetic interactions become dominating at lower volumes, leading to magnetic frustration effects. Similar results were derived earlier for pure fcc Fe by Sabiryanov *et al.*,[42] whereas Lagarec and Rancourt[43] presented a general consideration of the consequences of magnetic frustration effects on the phenomenology of FeNi Invar. In the present paper, we will return to the problem of the low-temperature magnetic states of Fe-Ni Invar alloys.

In an earlier attempt for a theory of the Invar effect, Kakehashi[44,45] used a semiempirical two-band correlated tight-binding model and a static single-site approximation within the functional integral approach. He showed that the Invar effect can be explained as a consequence of a reduction of the local moments of Fe with temperature caused by magnetic disorder effects. Recently, similar results[46] have also been obtained in the dynamical version of this approach.

Disordered local moment (DLM) calculations within the LSDA[47] for the paramagnetic state above the magnetic ordering temperature[48] have shown that the equilibrium volume of the paramagnetic state in Fe-Ni Invar alloys is smaller than that in the ferromagnetic state. They have also shown that the local magnetic moment of Fe is reduced compared to that in the ferromagnetic state. The same results have also been recently obtained by Lagarec *et al.*[19] in the LSDA LMTO-CPA calculations. The reduction of the magnetic moment in the DLM state accompanied by the corresponding reduction of the alloy equilibrium volume relative to that in the ferromagnetic (FM) state has also been obtained in first principles DLM calculations of disordered[49] and ordered[50] fcc Fe-Pt and bcc Fe-Co (Ref. 51) alloys as well as in Gd.[52] These calculations have also accurately reproduced the value of the anomalous spontaneous volume magnetostriction, ω_s, which describes the magnetic contribution to the thermal expansion.

The DLM formalism, however, has produced quite controversial results for Fe-Ni Invar alloys. For instance, Akai and Dederichs[53] have reported that in $Fe_{65}Ni_{35}$ the DLM state has an even lower total energy than the FM one. This result is in agreement with the above mentioned prediction[12] of unstable collinear ferromagnetic states, and the reason for both of these results is again the application of the LSDA. At the same time, the DLM state in $Fe_{65}Ni_{35}$ has a higher energy than the FM in the LSDA calculations by Johnson and Shelton.[54] These authors have also proposed that atomic short-range chemical order (ASRO) effects should be taken into account.

Exploiting this idea, Crisan *et al.*[55] calculated the thermal expansion of Fe-Ni Invar alloys using the Debye-Grüneisen model. The ASRO effects in this work have been modeled by using a partially ordered alloy in the total energy calculations. Although the description of the thermal expansion appears to be in fair agreement with experiment, there remains the contradiction that according to experiment[56] ASRO effects are essentially negligible for this system so that this point needs further investigations, besides the calculations have been done using the LSDA, which significantly underestimates the equilibrium volume of Fe-Ni alloys.

As follows from the presented above discussion, there is an apparent controversy between first principles results for

Fe-Ni Invar alloys: (i) the importance of ASRO for the Invar effect in $Fe_{65}Ni_{35}$ alloys and (ii) the fact that all previous calculations of the zero-temperature magnetic state have been done for too small lattice spacings and therefore the obtained magnetic state and magnetovolume properties do not correspond to the experimental situation. Therefore, in the present paper we investigate the ASRO in Fe-Ni Invar alloys, then we perform supercell calculations of the magnetic state at several volumes, close to and below the experimental one, and finally we calculate the spontaneous volume magnetostriction using the generalized gradient approximation for the exchange-correlation energy, which fairly accurately reproduces the equilibrium volumes.

II. METHODS AND DETAILS OF CALCULATION

Electronic structure and total energy calculations of Fe-Ni alloys have been performed by three methods: (i) the Korringa-Kohn-Rostoker Green's function method in the atomic sphere approximation (KKR-ASA),[57,58] (ii) the locally self-consistent Green's function (LSGF) method,[59] based on the KKR-ASA method, and (iii) the exact muffin-tin orbital (EMTO) method.[60] The CPA has been used in the electronic structure calculations of random alloys by EMTO and KKR-ASA methods. In order to get an accurate description (within the error of the exchange-correlation energy approximations) of the ground state properties,[38] the full-charge density (FCD) formalism[60] has been used in the EMTO calculations.

The electronic structure and total energy of random alloys in the single-site homogeneous EMTO(KKR-ASA)-CPA calculations have been obtained with the on-site screened electrostatic potential V^i_{scr} and energy E^i_{scr} (Ref. 61):

$$v^i_{scr} = -e^2\alpha_{scr}\frac{q_i}{S}, \tag{1}$$

$$E^i_{scr} = -e^2\frac{1}{2}\alpha_{scr}\beta_{scr}\frac{q_i^2}{S}. \tag{2}$$

Here, q_i is the net charge of the atomic sphere of the ith alloy component, S the Wigner-Seitz radius, and α_{scr} and β_{scr} the on-site screening constants. Their values, which are $\alpha_{scr}=0.8$ and $\beta_{scr}=1.15$, have been determined from the corresponding supercell LSGF calculations of a random $Fe_{65}Ni_{35}$ alloy.[61]

The basis functions in all calculations have been expanded up to $l_{max}=3$. We have also taken into account multipole moment contributions to the electrostatic energy. The summation over multipole moments for the electrostatic part of the one-electron potential and total energy has been carried out up to $l^M_{max}=6$. The integration over the irreducible part of the Brillouin zone has been performed over at least 1505 k points using the Monkhorst-Pack scheme.[62]

III. ATOMIC STRUCTURE OF INVAR ALLOYS

As already mentioned above, x-ray diffraction experiments[56] show that Fe-Ni Invar alloys exhibit very little atomic short-range order. At the same time, according to experimental data, there are at least two ordered phases in fcc Fe-Ni alloys: $L1_2$-Ni_3Fe and $L1_0$-FeNi.[63] The latter one has been found in meteorite specimens[64] and it is quite possible that it is metastable.[64,65] Therefore, there is a controversy between existing experimental data or their interpretations, which should be solved since the underlying atomic configuration is very important for basic ground state properties, as has been shown by Crisan *et al.*[55]

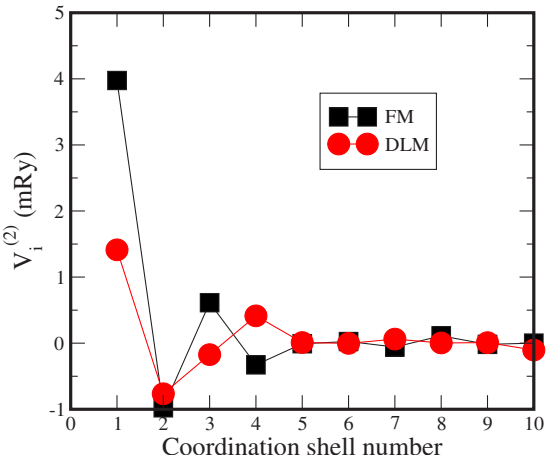

FIG. 1. (Color online) Effective pair interactions in $Fe_{65}Ni_{35}$ obtained for the ferromagnetic (FM) and paramagnetic (DLM) states.

We investigate this problem theoretically by using Monte Carlo simulations of the ordering effects. For this purpose, we first obtain effective interactions of the corresponding Ising-type Hamiltonian for fcc Fe-Ni alloys by using the screened generalized perturbation method (SGPM).[61,66,67] The effective pair SGPM interactions are determined as[61,66,67]

$$V_i \equiv V(\mathbf{R}) = V^{one-el}(\mathbf{R}) + V^{scr}(\mathbf{R}), \tag{3}$$

where V_i is the SGPM interactions at the ith coordination shell, given by a set of vectors $\mathbf{R}$, $V^{one\text{-}el}(\mathbf{R})$ the one-electron contribution to the SGPM interaction, and $V^{scr}(\mathbf{R})$ the screened electrostatic interaction:

$$V^{scr}(\mathbf{R}) = e^2\alpha_{scr}(\mathbf{R})\frac{q^2_{eff}}{S}. \tag{4}$$

Here, $\alpha_{scr}(\mathbf{R})$ are the intersite screening constants.[61,67] Their values have been determined from the corresponding supercell calculations, and for the first six coordination shells they are: 0.1083, −0.0065, −0.0065, −0.0003, 0.0008, and 0.0013. The screening constants for more distant coordination shells are very small and therefore the contribution from the corresponding screened Coulomb interactions can be neglected.

In Fig. 1, we show the pair effective interactions in the $Fe_{65}Ni_{35}$ random alloy obtained in the EMTO-CPA-GPM calculations at the experimental lattice spacing for two different magnetic configurations: FM and paramagnetic as it is given by the DLM model. As one can see, the magnetic state strongly influences the chemical interactions in this system:

TABLE I. Ordering energies (in mRy/at.) of $Fe_{50}Ni_{50}$ alloy in the FM and DLM states obtained from the SGPM interactions and in the direct total energy calculations.

	DLM state		FM state	
Structure	SGPM	E_{tot}	SGPM	E_{tot}
$L1_0$	−1.09	−0.60	−4.65	−4.42
CH ("40")	−1.45	−0.62	−2.03	−1.44

The nearest-neighbor effective pair interaction is substantially reduced in the DLM state compared to that in the FM state. One can also notice the change in the behavior of the effective pair interactions at the third and fourth coordination shells. As we will see below, this leads to a change of the ordering behavior in this system.

The magnetic state also affects the three- and four-site effective interactions: The interactions, which are relatively strong in the FM state, become quite weak in the DLM state. For instance, the three-site interaction for the triangle of nearest neighbors (which is the strongest in this system) is 0.95 mRy in the FM state, while it is only 0.02 mRy in the DLM state. A similar reduction is also found for the strongest four-site interaction for the nearest-neighbor tetrahedron, which is 0.53 mRy for the FM state and 0.1 mRy for the DLM state.

In order to check how accurately the SGPM effective interactions can reproduce the ordering effects, we have calculated the SGPM interactions for equiatomic alloy compositions in the DLM and FM states, and then from their values obtained the ordering energy[68] of the $L1_0$ and so-called CH (or "40" the definition of this structure can be found in Ref. 69) ordered phases at the lattice spacing of 3.59 Å. We have also calculated the ordering energies of these structures directly by the KKR-ASA method (the total energy of random fcc $Fe_{50}Ni_{50}$ alloys has been determined in the corresponding supercell LSGF calculations). The results are presented in Table I. It can be seen that the agreement between the SGPM results and direct total energy calculations is very good: The SGPM interactions only slightly overestimate the ordering tendency. They also correctly predict a switch of the type of ordering behavior from $L1_0$- to the CH-type due to the change of the magnetic state, although the SGPM interactions apparently overestimate the stability of the CH phase.

Since the SGPM interactions work reasonably well for this system, we have performed Monte Carlo simulations with FM and DLM SGPM interactions for $Fe_{50}Ni_{50}$ alloy. The FM interactions yield an ordering phase transition into the $L1_0$ structure at about 1000 K. The ordering temperature should be overestimated since (i) the SGPM interaction overestimates the ordering energy and (ii) we have neglected the effect of local lattice relaxations in the random state. The latter should, however, be small due to smallness of the local lattice relaxations.[56] The DLM effective interactions lower the ordering transition temperature to approximately 220 K (again this temperature should be overestimated) and the ordered phase has the CH structure. This means that in real life, the ordering phase transition in the $Fe_{50}Ni_{50}$ alloy can happen only well below the Curie temperature (close to 800 K at this composition), when the ferromagnetic order is strong enough. This is in agreement with some experimental evaluation of the Fe-Ni phase diagrams, according to which the $L1_0$ phase forms below 600 K.[70]

It is obvious that the magnetic state, in a similar way, should influence the atomic ordering in Fe-Ni Invar alloys (there is also an experimental evidence for the inverse effect, the influence of ASRO on the magnetic transition temperature in Invar alloys[71]). Thus, in order to find out the ASRO in real Fe-Ni Invar alloys, we have to find first the *relevant* magnetic state, under influence of which this ASRO is formed. The latter is determined by the heat treatment of Invar alloys and the atomic diffusion at the corresponding temperatures. Since Fe-Ni Invar alloys are usually annealed (for a rather long time) at temperatures about 1000 K (see, for instance, Ref. 72), one can conclude that they are formed above the Curie temperature, which, depending on the alloy composition, can vary between 400 and 500 K, i.e., in the *paramagnetic* state.

Monte Carlo simulations for $Fe_{65}Ni_{35}$ alloy with the corresponding DLM SGPM effective interactions show that the ASRO at 1000 K is, in fact, relatively small. The largest values of the Warren-Cowley SRO parameters are approximately −0.05 and 0.03 for the first and second coordination shells, respectively. Let us note that the corresponding experimental values are much less, −0.003 and 0.000. Partly, this difference originates from an overestimated ordering tendency by the SGPM interactions, and partly from unaccounted local relaxation effects in the Monte Carlo simulations. However, it is clear that these theoretical values can be considered as an upper limit of the SRO effects. Let us also note that the ASRO in Fe-Ni alloys in the DLM state is of ordering type (not clustering, as has been found in the calculations by Crisan *et al.*[55] for the LSDA equilibrium lattice spacing); however, the ordering transition temperature is only 150 K. This means that at 1000 K, the Fe-Ni alloys are too far away from an ordered state to be considered as partially ordered.

In the FM state, however, the situation is different. In the Monte Carlo simulations for $Fe_{65}Ni_{35}$ with the corresponding FM SGPM effective interactions, we find two phase transitions: one at about 520 K from a random phase to a partly ordered-$L1_0$ structure, and the other where the latter structure then decomposes into pure Fe and an ordered phase at about 250 K (on a fixed fcc lattice). Although this transition is very close to the Curie temperature of Fe-Ni Invar alloys (400–500 K), the effective interactions can get their full strength only at much lower temperatures, where the magnetization is close to 1. At these temperatures, however, there is practically no diffusion and this means that Fe-Ni Invar alloys remain in the random state with a relatively small amount of ASRO. The only way to make possible atomic rearrangements at low temperatures during a short time is to introduce a substantial amount of point defects. Indeed, traces of ordering has been found in Fe-Ni Invar alloys after electron irradiation at room temperature.[73]

IV. LOCAL MAGNETIC STRUCTURE OF Fe-Ni INVAR ALLOYS

As has been mentioned in the Introduction, there is experimental evidence that in spite of the fact that Fe-Ni Invar alloy is a ferromagnetic system, the ferromagnetic state is not homogeneous: That is, there are Fe atoms having an antiferromagnetic alignment of the magnetic moments. This inhomogeneity is a local environment effect, which means that in order to reproduce it in first principles calculations, one has to model these alloys by a large enough supercell, which allows for the corresponding fluctuations of the local chemical composition. To investigate the zero-temperature *collinear* magnetic state of $Fe_{65}Ni_{35}$, we have generated a 560-atom supercell with randomly distributed Fe and Ni atoms. The electronic structure and total energy calculations have been done by the LSGF method.[59] To take into account the local environment effects, the local interaction zone in the LSGF calculations included the atoms at the nearest-neighbor coordination shell. In some calculations, we also included the next nearest neighbors, which, however, had only little effect on the resulting magnetic state.

The LSDA-LSGF supercell calculations for $Fe_{65}Ni_{35}$ at the *experimental* lattice spacing (a=3.59 Å, or Wigner-Seitz radius S_{WS}=2.65 a.u.) have shown that finding the lowest energy (collinear) magnetic configuration is a nontrivial problem. Different initial conditions, such as a supercell setup or the value of a mixing coefficient in the self-consistent procedure, lead to different distributions of magnetic moments, although the final global state is always ferromagnetic, with some local antiferromagnetically aligned magnetic Fe moments. These antiferromagnetically aligned moments occur on Fe sites, which have only one or no Ni neighbors. It is interesting to note that while the average value of the magnetic moment of Fe atoms with the FM orientation (FM Fe) is 2.43 μ_B, it is only (−)1.64 μ_B for the AFM orientation (AFM Fe). We also find that the distribution range of the magnetic moments around the average value is rather large and amounts to ±0.6 μ_B. All Ni atoms have a FM orientation of the magnetic moment with an average value of 0.637 μ_B. Taking into consideration that the concentrations of the FM and AFM Fe atoms in the calculations were 62.4 and 2.6 at. %, respectively, the average value of the global magnetic moment is 1.70 μ_B, which is in very good agreement with the experimental data, 1.75 μ_B.[28]

The appearance of the antiferromagnetically aligned magnetic moments on Fe atoms can be understood as the result of locally frustrated exchange interaction parameters found recently in calculations for FeNi alloys.[41] However, a strong dependence of the atomic magnetic moments on the local atomic environment, revealed in the present calculations, casts some doubts on the overall validity of the Heisenberg-like parametrization of the magnetic energy.

A change of the lattice spacing in the vicinity of the experimental value induces a change of the magnetic ground state. For a slightly larger lattice spacing, a=3.62 Å (S_{WS} =2.675 a.u.), we find in the LSDA calculations only two AFM Fe atoms in the supercell, and the average magnetic moment becomes 2.52 μ_B on Fe and 0.65 μ_B on Ni, so that the average magnetic moment rises to 1.86 μ_B. Vice versa, for slightly smaller lattice spacing, a=3.55 Å (S_{WS} =2.625 a.u.), the ferromagnetic state is only marginally stable. The (LSDA) energy difference between two states with an average magnetic moment of 1.36 and 0.34 μ_B is only 0.1 mRy/atom. In the latter case, the magnetic state is actually a mixture of clusters with AFM alignment of spins, including Ni atoms, i.e., it can hardly be called ferromagnetic. It is obvious that some general noncollinear alignment for the magnetic structure would be needed in this case, which is beyond the scope of the present work.

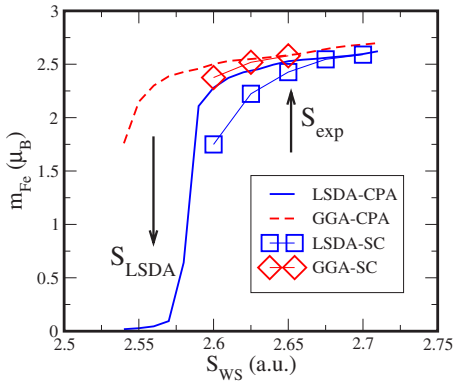

FIG. 2. (Color online) Average local magnetic moment on FM Fe atoms in $Fe_{65}Ni_{35}$ obtained in KKR-CPA (CPA) and supercell (SC) LSGF calculations using the LSDA and GGA as a function of Wigner-Seitz radius. The experimental Wigner-Seitz radius as well as the equilibrium LSDA values are shown by the arrows.

According to the LSDA picture, the uniform ferromagnetic state is unstable in Fe-Ni Invar alloys at the experimental lattice spacing, although the degree of the inhomogeneity of the ferromagnetic state predicted by the LSDA is quite small. An examination of the binding energy curves from noncollinear calculations by van Schilfgaarde *et al.*[12] performed for a 36-atom supercell of the Fe-Ni Invar alloy shows that the experimental value of the lattice constant a =3.59 Å is just above the region where metastable noncollinear states exist. However, this cannot rule out that there might exist a stabilization of some local noncollinear states if a larger supercell would have been used in calculations to model chemical disorder more properly.

In contrast to the LSDA, the generalized gradient approximation (GGA)[74] LSGF calculations give a homogeneous ferromagnetic state (i.e., without locally frustrated AFM Fe atoms) at the experimental lattice spacing with the average magnetic moment of about 1.85 μ_B/atom. The AFM Fe atoms in Fe-rich local environment appear only at lower volumes (in our calculations for a=3.55 Å, although we do not know where exactly a crossover from a homogeneous to an inhomogeneous FM state happens). In Fig. 2, we show our results for the average local magnetic moment on FM Fe atoms obtained in the LSDA and GGA calculations using the KKR-CPA method (where local environment effects are neglected) and in the LSGF supercell calculations. First of all, one can clearly see that the local environment effects can strongly influence the value of the local magnetic moment, although at the experimental Wigner-Seitz radius the effect is relatively small in the LSDA and has completely disappeared

in the GGA. This observation suggests that CPA mean-field-like description might still provide a good background for modeling magnetovolume effects in $Fe_{65}Ni_{35}$ associated with finite-temperature magnetic excitations.

V. ANOMALOUS VOLUME MAGNETOSTRICTION IN THE MEAN-FIELD CONSIDERATION

It is well known that the LSDA significantly underestimates the equilibrium volume of $3d$ metals.[36–38] In the case of fcc $Fe_{65}Ni_{35}$, it yields equilibrium lattice constant $a=3.495$ Å, while the experimental value is 3.59 Å. Nevertheless, almost all the earlier first principles calculations of Fe-Ni Invar magnetovolume properties have been done in the LSDA. In contrast to the LSDA, as will be shown below, the GGA yields the equilibrium lattice constants in good agreement with the experimental data, and thus could also be able to produce reasonable magnetovolume properties. In particular, we will use it here for the calculations of the ground state properties and spontaneous volume magnetostriction, ω_s, which has an anomalously large experimental value.

The spontaneous volume magnetostriction, ω_s, is defined as

$$\omega_s = \frac{\Omega_{FM} - \Omega_{PM}}{\Omega_{PM}}, \tag{5}$$

where Ω_{FM} and Ω_{PM} are zero-temperature volumes for the FM and paramagnetic states. For Invar systems, it is anomalous and positive, which is the only unique common feature of all metallic Invar systems, whereas all the other physical anomalies found in various Invar alloys and compounds are material specific.[2] Thus, any theory of the Invar effect should explain or predict on a quantitative level the anomalous value of ω_s.

If longitudinal spin fluctuations are neglected, the paramagnetic state above T_c can be viewed as a random mixture of atoms with randomly oriented magnetic moments and zero total magnetization, i.e., as a DLM state.[48] The DLM model for the paramagnetic state has been successfully used for the prediction of the anomalously large values of ω_s in ordered and disordered Fe-Invar alloys with Pt, Pd, and Co.[49,51] Moreover, it also could predict the vanishing anomalous magnetic contribution to the thermal expansion for non-Invar compositions of the same alloys and thus to link the Invar effect to the decrease of the local atomic moments of Fe in the paramagnetic state due to effects of thermal magnetic disorder.

Here, we calculate the spontaneous volume magnetostriction of $Fe_{65}Ni_{35}$ using the CPA, i.e., in the mean-field description of random alloys neglecting local environment effects. Although the latter are important to obtain the correct zero-temperature magnetic structure and ground state properties, our treatment still provides an important estimate and after all the amount of the AFM frustrated Fe atoms has found to be only about 2%–3%. In fact, we have checked that supercell LSGF calculations produce practically the same equilibrium volume as the usual homogeneous KKR-ASA-CPA, where the presence of the AFM fluctuation is neglected. However, in order to avoid errors due to the ASA for the electrostatic energy, we use the EMTO-CPA-FCD method, which proved to be quite accurate for the ground state properties,[38] for the calculations of the spontaneous volume magnetostriction.

The calculated equilibrium lattice spacing in the FM ground state is 3.592 Å ($S_{WS}=2.6525$ a.u.). The (zero-temperature) equilibrium lattice spacing in the DLM state is 3.553 Å ($S_{WS}=2.624$ a.u.), which yields the GGA mean-field value of $\omega_s=3.2\%$. This is 50% larger than the experimentally estimated value of 2.2%.[75] Thus, similar to the other Fe based alloys the Invar effect can be predicted also for Fe-Ni alloys by DLM calculations. The calculated bulk modulus in the FM state is 177 GPa, which is, however, much higher than the corresponding experimental value of 117 GPa obtained from the ultrasonic measurements.[40] We do not know the origin of this difference, although there exist some speculations[17] that the value of the bulk modulus could be underestimated in ultrasonic measurements due to softening of the longitudinal phonon modes.

Although the GGA works very well for the ground state properties of the $3d$ metals and their alloys, it, on the other hand, slightly overestimates the stability of the ferromagnetic state (and stability of the local moment, in general), at least in the case of the PBE96 implementation.[74] A possible way to combine the best of the LSDA and GGA is to use the LSDA self-consistent density and magnetic moments (also obtained in the CPA-mean-field consideration without AFM frustrations) in the GGA total energy calculations (LSDA-GGA), i.e., just recalculating the exchange-correlation energy in the GGA. Such a combination is justified by the fact that both approximations produce practically indistinguishable electronic structure of the valence states responsible for the interatomic bonding, and the fact that the difference in the description of the ground state properties originates mainly from the strong gradient corrections for the electron density in the core region, close to the atomic nuclei, which has no direct connection to the magnetism and bonding.

In Fig. 3, we show the results for the GGA total energies of the FM and DLM random $Fe_{65}Ni_{35}$ alloy obtained in the EMTO-CPA-FCD calculations. One can see that despite the differences in the values of magnetic moments in the GGA and LSDA self-consistent calculations, there is very little difference in the behavior of the GGA total energies. All the equilibrium volumes change very little and the value of ω_s in such calculations is 3.09%.

Nevertheless, there is at least one important change; the value of the "isotropic" Grüneisen constant (or equivalently dB/dP) substantially increases in the DLM state, from 1.43 in the GGA calculations to 1.97 in such LSDA-GGA calculations. The latter actually provides enough thermal lattice expansion (in the simple Debye-Grüneisen model) for an alloy in the DLM state to have at 500 K the same lattice spacing as in the pure FM at 0 K, and therefore indicates that even a large theoretical value of ω_s is still reasonable in order to get the proper thermal expansion properties. In doing so, we, of course, neglect a possible contribution from longitudinal spin fluctuations to the thermal expansion of the (partially) paramagnetic phase. It should also be noted that the so-called "experimental" value is, of course, an estimation,

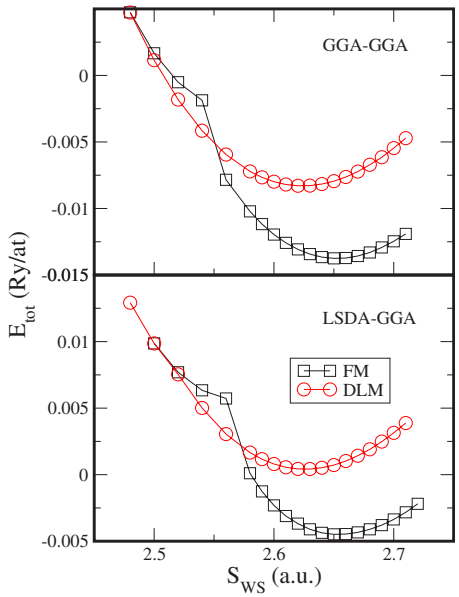

FIG. 3. (Color online) GGA total energy of FM and DLM $Fe_{65}Ni_{35}$ obtained in the EMTO-CPA-FCD calculations. On the top panel, we show the result of self-consistent calculations within the GGA (GGA-GGA), and on the bottom panel those within the LSDA (LSDA-GGA).

based on the extrapolation of the thermal expansion curve from the high-temperature paramagnetic state down to the zero temperature, so it can also be in error.

Let us finally point out that the decrease of the equilibrium volume in the paramagnetic DLM state is due to a decrease of the local magnetic moments relative to those in the ferromagnetic state. The GGA (LSDA) calculated moments at the equilibrium lattice constant in the FM state are 2.58 (2.51) and 0.63 (0.65) μ_B for Fe and Ni, respectively, while in the DLM state the local moment on Fe site is 2.20 (2.00) μ_B and zero on Ni (one can also notice a large difference between the GGA and LSDA magnetic moments in the DLM state). Thus, the origin of the Invar effect in $Fe_{65}Ni_{35}$ is most likely to be the same as in other Invar systems such as fcc Fe-Pt and bcc Fe-Co, although the latter alloys do not have such rich and complex physical properties as Fe-Ni.[76,77]

VI. CONCLUSIONS

Our calculations show that the ASRO effects at the experimental lattice spacing are very weak. Nevertheless, local environment effects are important for an accurate first principles description of real Fe-Ni Invar alloys since they lead to local magnetic instabilities of the global ferromagnetic state just at the experimental equilibrium (zero-temperature) volume. The inclusion of such local effects, which are due to local fluctuations of the alloy configuration, can be done only for quite large systems, consisting of at least hundreds of atoms. At the same time, the amount of such antiferromagnetically frustrated atoms or clusters is very sensitive to the volume near its equilibrium value.

The LSDA hugely underestimates a ground state volume in $Fe_{65}Ni_{35}$ and thus is not a suitable choice for a description of the magnetovolume effects in this system, since the calculated lattice constant falls into the region where antiferromagnetic interactions play a dominant role, creating frustrated globally noncollinear magnetic structures. At the experimental lattice constant, which is well reproduced by GGA, the noncollinear states may exist only locally at a small fraction of Fe sites which do not have Ni atoms as nearest neighbors.

Our GGA mean-field-like EMTO-CPA calculations of the ground state properties of $Fe_{65}Ni_{35}$ alloys show that it is possible to get a reasonable value for the spontaneous volume magnetostriction, which can at least qualitatively and even semiquantitatively explain the Invar effect, even though the reported experimental value is overestimated by 50%. Therefore, we advocate the conclusion that the origin of the thermal expansion anomaly in the Fe-Ni Invar alloys is not directly connected to their peculiar properties such as magnetovolume instability at high applied pressures, low-temperature anomalies in the ac susceptibility, phonon softening, etc. That is, the physical origin of the Invar effect in Fe-Ni alloys is most likely to be similar to that in the other alloys and materials, which do not have such peculiar physical properties as their Fe-Ni counterparts. This point, however, needs further theoretical investigation, which should include the proper treatment of finite-temperature magnetism in the $Fe_{65}Ni_{35}$ Invar alloy as well as its influence on the equilibrium properties of the alloy.

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