Laves-phase (Zr,Nb)Fe_2 alloys as model Invar systems without magnetic frustration: Comparison to Fe-Ni Invar

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We calculate the spontaneous volume magnetostriction and exchange interaction in C15 Laves-phase $(Zr_{1-x}Nb_x)Fe_2$ alloys, which exhibit a distinctive Invar-type anomaly in their thermal expansion. Our first-principles study is based on the disordered local-moment approximation and the magnetic force theorem applied in the framework of the local spin-density approximation and the Korringa-Kohn-Rostoker band-structure method. The theory presented is able to predict the qualitative difference in the thermal expansion between the systems considered. The exchange interactions in $(Zr_{1-x}Nb_x)Fe_2$ and in classical Fe-Ni Invar alloys have been recalculated and compared in a wide range of volumes. We find that the magnetic interactions in $(Zr_{1-x}Nb_x)Fe_2$ do not become frustrated at lower volumes contrary to the case of Fe-Ni Invar alloy. Thus, it is explicitly shown that antiferromagnetism and magnetic noncollinearity at low volumes are not a prerequisite for an Invar anomaly to occur.

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I. INTRODUCTION

Recent developments in the understanding of the origin of the Invar anomaly (i.e., an anomalously small lattice thermal expansion below the magnetic ordering temperature[1] in some magnetic metallic materials) have taken place due to the application of the state-of-the-art first-principles methods of band-structure calculations. There are, however, two different lines for the explanation of the Invar effect based on the results of *ab initio* simulations. One is related to the "classical" Fe-Ni Invar alloy and to the observation that at some volumes lower than equilibrium in the Fe-Ni Invar alloy the ferromagnetic (FM) state become unstable with respect to some new antiferromagneticlike phases (see recent study and discussion in Ref. 2). The quantitative description of the anomalous magnetic contribution to the thermal expansion along this line is still lacking. Similar ideas were expressed much earlier, e.g., in the phenomenological theory by Kondorskij and Sedov[3] (see also Rancourt *et al.*[4,5]). The direct calculations of the interatomic magnetic exchange interactions in Fe-Ni alloys using the first-principles magnetic force theorem indeed have shown[6] that Fe-Fe interactions change from ferromagnetic to antiferromagnetic for decreasing volume causing magnetic frustration effects on the fcc lattice. The strong decrease in the ferromagnetic exchange coupling with volume and the change in its sign in pure fcc Fe have been observed also in an earlier seminal work by Sabiryanov *et al.*[7] (See also the study of the related ternary fcc Fe-Ni based alloys.[8])

We note that the simple Weiss two-state model,[9] which is still often used as reference Invar model in some experimental[10,11] and sometimes even in theoretical papers[12] cannot be advocated by first-principles results since the celebrated two separated total-energy minima, which appear in earlier calculations[13,14] are just the consequence of disregarding the possibility for antiferromagnetism at low volumes (see discussion in Ref. 15). Another line of the development considers the anomalous negative contribution to the thermal expansion in Invar systems as consequence of a reduction in the equilibrium volume due to a thermally induced decrease in the local atomic magnetic moments.[1] Kakehashi[16] developed a semiempirical version of this approach in the framework of the theory of the spin fluctuations. At certain conditions[17] the decrease in the local moments becomes anomalously large and the system exhibits an Invar behavior. The decrease in the local moments with temperature is a consequence of thermal magnetic disorder. We call this scenario of the Invar effect as "magnetostrictive" theory of Invar. It has been shown that it is possible to reach a quantitative description of the spontaneous volume magnetostriction for a wide class of Invar materials[17–20] by properly modeling the paramagnetic state above the magnetic ordering temperature in first-principles calculations. These investigations have been based on modeling the paramagnetic state using the disordered local-moment (DLM) approximation introduced in the framework of the local spin-density approximation (LSDA) by Gyorffy *et al.*[21] Johnson *et al.*[22] pioneered the application of the DLM model to Fe-Ni Invar alloys. It is important that the formalism based on the DLM method allows to predict the Invar behavior in the Invar-type alloys and also the absence of the effect in non-Invar alloy compositions (such as in fcc Fe-Pt and bcc Fe-Co).[17] Although the application of the DLM formalism to Fe-Ni Invar alloy leads to somewhat overestimated values of the spontaneous volume magnetostriction as compared to experiment, the magnetostrictive theory of the Invar effect seems to be validated on a first-principles basis even in this case.[23,24]

Despite that the magnetostrictive theory of the Invar effect is successful for many different Invar materials it is difficult to rule out completely the "antiferromagnetic" scenario, in particular, for Fe-Ni Invar alloys. In this paper we undertake a first-principles study of the Invar-type C15 Laves phase $(Zr_{1-x}Nb_x)Fe_2$ alloys where, as we will show, the ferromagnetic character of the exchange interactions does not change with decreasing volume. Moreover, the ferromagnetic coupling constant becomes even stronger under a reduction in the interatomic distance.

The distinctive Invar-type anomaly in the thermal expansion of $(Zr_{0.7}Nb_{0.3})Fe_2$ has been reported long ago.[25] The intermetallic phase $ZrFe_2$ exhibits the largest value of the spontaneous volume magnetostriction, $\omega_{s0}=1\%$, among the Fe-based Laves-phase intermetallics.[26] When Nb is alloyed for Zr the Curie temperature decreases but ω_{s0} remains almost constant and a pronounced Invar-type anomaly in the thermal expansion is developed resulting in an almost vanishing thermal expansion visible in the experiment.[25] On a phenomenological level the magnetostrictive theory explains the Invar effect in $(Zr_{1-x}Nb_x)Fe_2$ alloys with Nb substitution.[1,25] To be consistent in proving the validity of the magnetostrictive model based on first-principles DLM calculations we also consider the isostructural compound YFe_2 where the spontaneous volume magnetostriction is found experimentally to be nearly zero.[26]

Although the class of Invar materials investigated here has been much less studied compared to the classical Fe-Ni and Fe-Pt systems it may be regarded as model system. In these alloys the magnetic Fe sublattice is fully ordered and substitutional Nb atoms appear only on the Zr sublattice. Thus, there is no chemical disorder on the Fe sublattice. In this respect it is an even more perfect example than ordered Fe-Pt, which we studied recently,[27] where some chemical disorder is always seen in experiment.[28] Our study here shows that the Nb substitution has almost no influence on the calculated value of ω_{s0} in $(Zr_{1-x}Nb_x)Fe_2$. However, the absolute value of ω_{s0} is overestimated in the calculations similar to our recent study of Fe-Ni Invar[24] and Fe-Cu.[29]

In addition to the study of the volume dependence of the interatomic magnetic exchange interactions in $(Zr_{1-x}Nb_x)Fe_2$ we have also revisited the calculations of exchange interactions in Fe-Ni alloys made by Ruban *et al.*[6] We employ the generalized gradient approximation (GGA) (Ref. 30) for exchange and correlation instead of the bare local spin-density approximation. Apart of the comparison with $(Zr_{1-x}Nb_x)Fe_2$, the reason for such revisiting is a recent study of Fe-Ni where it has been shown[24] that only the GGA approach leads to a reasonable description of the ground-state volumes in Fe-Ni.

II. METHOD OF CALCULATIONS

Our total-energy calculations are based on the local spin-density approximations and the generalized gradient corrections (GGA) to the exchange and correlations functional in the form proposed by Perdew, Burke, and Ernzerhof.[30] The band structure is calculated using a bulk Korringa-Kohn-Rostoker (KKR) method within the atomic-sphere approximation (ASA) as described in Refs. 31 and 32. The effects of chemical disorder due to Nb substitutions for Zr were treated using the conventional coherent-potential approximation (CPA). The partial waves in the KKR-ASA calculations have been expanded up to $l_{max}=3$ ("*spdf*" basis) inside the atomic spheres. The total energy was calculated using multipole screening electrostatic corrections to the electrostatic potential and energy (up to $l=6$) as described in Ref. 33. All calculations were performed within the scalar relativistic approximation, which contains all relativistic effects with the exception of spin-orbit coupling. The disordered local-moment approximation is used to model a paramagnetic state above the Curie temperature in the framework of CPA as described by Gyorffy *et al.*[21] The relative difference between the equilibrium volumes of the ferromagnetic and DLM states defines a spontaneous volume magnetostriction.[17,18]

The interatomic magnetic interactions between the Fe moments have been calculated using the magnetic force theorem based on the Green's-function technique[34] in a similar fashion as has been done earlier for Fe-Ni Invar alloy[6] (see Ref. 35 for details of the implementation in the KKR-ASA formalism). The total-energy and band-structure calculations where converged using 285 (nonequivalent k points in the irreducible wedge of the Brillouin zone of the fcc structure, whereas for magnetic exchange calculations this number has been increased to 4381 nonequivalent k points.

III. RESULTS AND DISCUSSION

The spontaneous volume magnetostriction, ω_{s0}, defined as the difference between the equilibrium volumes of the paramagnetic state above the Curie temperature T_c and the ferromagnetic ground state at $T=0$ K, is a key physical quantity which characterizes the difference between Invar and non-Invar metallic systems.[1] Moreover, as mentioned in the review by Shiga,[1] its anomalously large values in Invar-type metallic alloys and compounds are the only common specific features of Invars—all other anomalies for physical properties accompanying the Invar effect are material specific. The equilibrium paramagnetic volume in this definition means the volume of the material in the paramagnetic state minus the contribution to the total volume associated with lattice vibrations. The exact experimental definition of this quantity is somehow biased since it includes a fitting of a "normal" (nonanomalous) thermal expansion in the paramagnetic state at high temperatures well above T_c toward zero temperature. The thorough description of the experimental determination of ω_{s0} can be found in Wasserman's[36] review on Invar alloys, which however shows that different methods give approximately similar results.

As in our previous work on Fe-based binary Invar alloys[19] we have use the DLM approach for modeling the paramagnetic state and to calculate the corresponding equilibrium volume. Then ω_{s0} can be calculated as

$$\omega_{s0}=\frac{V(\mathrm{FM})-V(\mathrm{DLM})}{V(\mathrm{DLM})}, \tag{1}$$

where V(FM) and V(DLM) are the *ab initio* calculated equilibrium volumes in the ferromagnetic and the DLM state, respectively. The results of the calculations are given in Table I. Concerning the ferromagnetic ground state our magnetic moments are in good agreement with earlier full-potential ground-state calculations[37,38] of $ZrFe_2$, where, in particular, the opposite direction of Zr induced magnetic moments to the Fe ferromagnetic matrix has been found. From the results in the table one sees immediately that this approach gives an overestimation of the ω_{s0} values by $\sim 1\%$ as compared to experiment. However, we note that this overestimation is about the same for $ZrFe_2$, $Zr_{0.7}Nb_{0.3}Fe_2$ and the

TABLE I. Calculated equilibrium volume given in terms of the average atomic Wigner Seitz radius (R_{ws}) in the FM and DLM state, spontaneous volume magnetostriction calculated and experimental (Ref. 26) and atomic magnetic moments at the corresponding equilibrium R_{ws} for Fe and A=(Zr or Y).

	R_{ws}(FM) (a.u.)	R_{ws}(DLM) (a.u.)	ω_{s0}(calc./expt.) (%)	m_{Fe}(FM) (μ_B)	m_{Fe}(DLM) (μ_B)	m_A(FM) (μ_B)
$ZrFe_2$	2.901	2.876	2.6/1.0	2.12	1.62	−0.84
$Zr_{0.7}Nb_{0.3}Fe_2$	2.872	2.843	2.5/0.8	2.04	1.57	−0.71
YFe_2	3.014	3.001	1.3/ ~0.0	2.24	2.06	−0.8

non-Invar compound YFe_2. The overestimation of ω_{s0} by approximately 1% using Eq. (1) has also been found in Fe-Ni (Ref. 24], Fe-Pt (Ref. 27) alloys, and cementite Fe_3C (Ref. 20). This overestimation is appears to be somewhat "systematic" in the sense that it is about the same for all alloy compositions. This allows us to still discriminate between Invar materials with an overall large value of ω_{s0} as compared to the non-Invar systems. Despite of this systematic error, our calculations correctly predict the development of a magnetovolume anomaly in Invar-type $Zr_{0.7}Nb_{0.3}Fe_2$ when compared to non-Invar YFe_2. The source of this "uniform" overestimation is not completely clear, it may be related to the uncertainty of experimental determination of ω_{s0}, e.g., to the extrapolation of the "normal" thermal expansion at high temperatures, well above T_c, down to low temperatures, which disregards changes in the bulk modulus caused by the magnetic order at low temperature. This important question should be investigated and discussed in the broader context of all Invar system but reaches beyond the scope of this paper.

Let us now turn to the comparison of the behavior of the magnetic interactions in $Zr_{0.7}Nb_{0.3}Fe_2$ and classical $Fe_{65}Ni_{35}$ Invar alloy under applied pressure. We calculate the interatomic interaction parameters J_{ij} of the Heisenberg-type Hamiltonian,

$$H = -\sum_{i,j\in\{\mathrm{Ni}\}} J_{ij}\vec{m}_i\vec{m}_j, \tag{2}$$

where $\vec{m}_i$ is the magnetic moment of the atom on the ith lattice site. The method is essentially similar to those used in Ref. 6 but GGA is employed instead of LSDA for to the reason explained above. However, our results are very similar to the previous work with the exception that our equilibrium lattice constant is closer to experimental.

For the magnetic interaction we restrict ourselves to the discussion of only the three nearest-neighbor (NN) shells since the Fe-Ni and Ni-Ni interactions are essentially ferromagnetic and almost volume independent in volume interval considered. The respective Fe-Fe exchange interactions are presented in the upper panel of Fig. 1. As the lattice constant decreases a dramatic change occurs in the first nearest-neighbor interaction, as at a certain volume this interaction becomes antiferromagnetic. On the lower panel it is shown that due to this the interaction parameter J_0, which is defined as a sum over all interactions connecting the given Fe site to the rest of the lattice sites (here we include Fe-Ni interactions as well), also becomes antiferromagnetic at lower volumes. However, this feature appears as a volume, which is far from the equilibrium volume, which is plotted as vertical line. Thus the at the experimental volume the ground state is dominantly ferromagnetic and effects of antiferromagnetic frustrations on the fcc lattice cannot be observed at the ambient pressures in these systems.

At this point one needs to mention an existing controversy between experiment and theoretical results published by van Schilfgaarde *et al.*[39] The manifold of the noncollinear states, that have been found in these calculations[39] to be lower in energy than collinear ferromagnetic configurations, has been never observed experimentally.[40–42] Now, after the discussion given above, it becomes apparent that the source of the controversy is the application of LSDA in the calculations presented in Ref. 39. LSDA predicts an equilibrium volume lower than the experimental one at ambient pressures and places the energy minimum with respect to the volume ex-

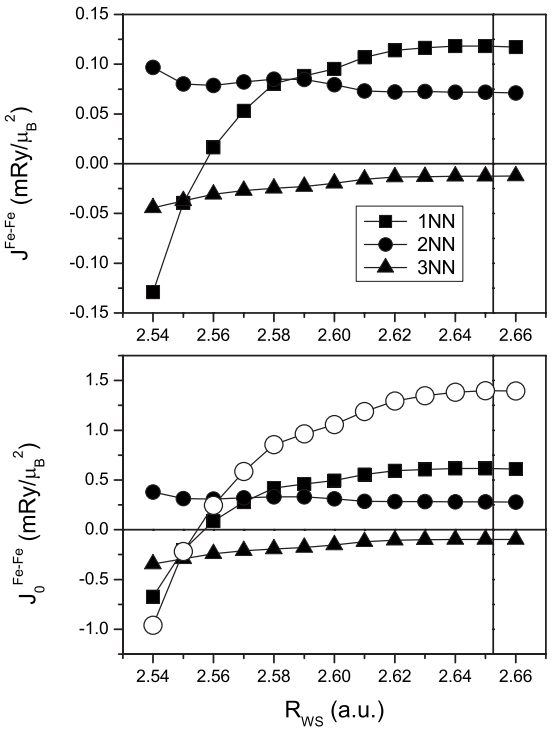

FIG. 1. Lattice-constant dependence of the interatomic exchange interactions in fcc $Fe_{65}Ni_{35}$. Upper panel: Fe-Fe exchange interaction constants for the first three NN shells. Lower panel: total exchange interaction constant J_0 for Fe site (open symbols) and for first three NN shells (full symbols), which provide the major contribution to J_0.

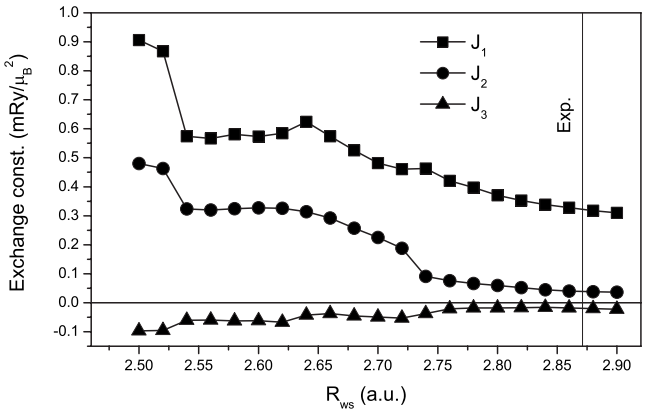

FIG. 2. Interatomic exchange interactions in C15$Zr_{0.7}Nb_{0.3}Fe_2$.

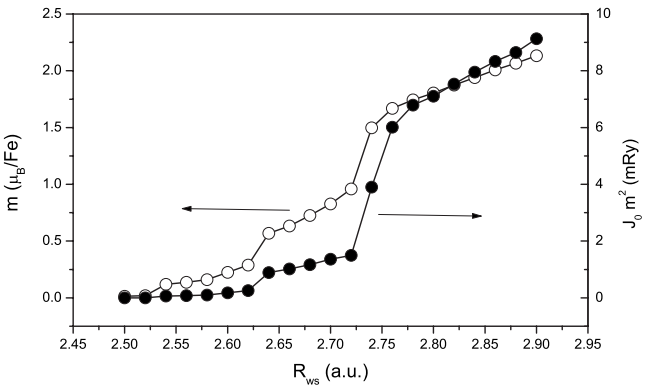

FIG. 3. Lattice-constant dependence of the magnetic moment of Fe in $Zr_{0.7}Nb_{0.3}Fe_2$ (open symbols) and of the product of the total interaction constants J_0 and square of Fe magnetic moment (full symbols).

actly in the region where Fe-Fe antiferromagnetic interactions start to become important. The application of GGA removes this controversy by placing the energy minimum inside the ferromagnetic region and at the same time yield a value of the equilibrium lattice constant close to experiment.[24] Thus, the claimed instability of the ferromagnetic configuration may occur only at high pressure. Indeed, experiments done for Fe-Ni Invar have demonstrated a stabilization of a spin-glasslike state at pressures at the order of a few gigapascals.[43]

The observation that there exists a volume region where the ferromagnetic state becomes unstable in the Fe-Ni alloys with respect of antiferromagnetism, raises a question concerning its relevance to the Invar phenomena. Such a scenario for the Invar effect based on this observation has been advocated.[39] However, the results of our study of the volume dependence of the exchange interactions in $Zr_{0.7}Nb_{0.3}Fe_2$ Invar-type systems presented below rule out any such model.

In Fig. 2 we show the calculated exchange constants for three nearest-neighbor shells in C15 structure of $Zr_{0.7}Nb_{0.3}Fe_2$. As can be seen, the leading ferromagnetic exchange interactions stay ferromagnetic as volume decreases from the experimental one. Their values even increase at lower volumes. By taking the sum over the first 50 shells to calculate the constant J_0 we find that its value stays positive until the magnetic moment vanishes. The ferromagnetic character of the system over the entire volume interval down to the stabilization of a paramagnetic state without spin polarization is further seen in Fig. 3. There we plot the lattice constant dependence of the magnetic moment and the product of J_0 and square of the moment of Fe. Thus, one may conclude that although $Zr_{0.7}Nb_{0.3}Fe_2$ exhibits a distinctive Invar-type anomaly, it does not exhibit any antiferromagnetic instability and is thus essentially different from Fe-Ni Invar.

IV. CONCLUSIONS

We have shown that $Zr_{0.7}Nb_{0.3}Fe_2$ does not show any antiferromagnetic instability at lower volume, although it has a distinctive Invar anomaly in its thermal expansion similar to Fe-Ni Invar, where such kind of instability occurs. This feature makes any "antiferromagnetic" scenario for the Invar effect questionable. The absence of chemical disorder in the magnetic Fe sublattice and the absence of magnetic frustration for any volume region allows to regard this material as model Invar-type system. Our discussion of the volume dependence of the Fe-Ni exchange constants points toward a solution of a long-standing speculation concerning any inconsistency of the experimental observation of the collinear ferromagnetic configuration at ambient pressures and earlier theoretical predictions of noncollinear magnetic order in Fe-Ni. The instability only occurs at low volumes, thus under high pressure. The source of the controversy is the application of the LSDA, which gives an energy minimum at a volume much lower than experiment—exactly in the volume region, where the antiferromagnetic Fe-Fe becomes important.

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