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Magnetostriction in Fe-based alloys and the origin of the Invar anomaly

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We show that for Fe-based alloys the spontaneous volume magnetostriction can be calculated from first principles in good agreement with experiment. Our results are obtained by modeling the paramagnetic state above the magnetic ordering temperature as a state with disordered local moments. Investigating bcc Fe-Co and fcc Fe-Pt(Pd) alloys which exhibit large values of the volume magnetostriction in a certain range of chemical composition and concomitantly an anomalously low thermal expansion coefficient (Invar effect), we find that this behavior is due to changes in the electronic structure induced by the effects of magnetic disorder leading to reduced local atomic moments in the paramagnetic state. The large values of the spontaneous volume magnetostriction found in Invar alloys scale with the equally observed large changes in the local moments.

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The spontaneous volume magnetostriction ω_s, defined as the relative volume difference between the magnetically ordered and the paramagnetic state, is a fundamental property of magnetic compounds and alloys and has attracted ongoing interest in solid-state physics.[1] It is thus not surprising that *ab initio* calculation of this quantity has always been considered to be a great challenge for conventional band-structure methods.[2] Since Janak and Williams,[3] on the basis of first-principles density-functional theory (DFT) calculations within the local spin-density approximation (LSDA) demonstrated the failure of the Stoner model for the magnetovolume effect in α-Fe, many attempts have been made to improve their results. This was undertaken either by applying more accurate methods based on other forms of the DFT (Ref. 2) or by going beyond the static Stoner approximation by including thermal spin fluctuations,[4] where it was shown that the main difficulties came from ignoring the existence of local moments in the paramagnetic state. The modeling of the paramagnetic state in band-structure calculations by simply assuming it to be nonspin polarized must inevitably lead to grossly overshooting values of ω_s in systems where well-defined local moments exist above the magnetic ordering temperature as in α-Fe.

To obtain a more realistic description of the paramagnetic state within first-principles calculations we apply the disordered local moment (DLM) picture of Cyrot[5] and Hubbard,[6] which has been reformulated in the language of LSDA-DFT by Gyorffy *et al.*[7] We employ this method to calculate ω_s for body-centered-cubic (bcc) Fe-Co and face-centered-cubic (fcc) Fe-Pt and Fe-Pd alloys, which in a certain range of chemical composition show anomalously small thermal expansion below the magnetic ordering temperature (Invar anomaly) (Refs. 8,9) and concomitantly large values of $\omega_s \approx 10^{-2}$. We find that the observed dependence of ω_s on the chemical compositions in these alloys can be very well predicted on the basis of *ab initio* DLM calculations and that our values of ω_s are in good quantitative agreement with the experimental estimates. Comparing the calculated values of the local magnetic moments in the ferromagnetic and the DLM state reveals a strong correlation between a large reduction of the Fe local moments in the paramagnetic DLM state and the high values of ω_s in Invar alloys. Outside the Invar composition range, e.g., in pure bcc Fe and fcc $Fe_{1-c}Pt(Pd)_c$ for <0.5, both ω_s and the reduction of the local moments are found to be small. For Fe-Pt alloys this approach has provided a quantitative description of the Invar effect.[10]

The electronic structure of disordered bcc $Fe_{1-c}Co_c$ ($c<0.6$), fcc $Fe_{1-c}Pt_c$ ($0.25<c<0.6$), and $Fe_{1-c}Pd_c$ ($0.3<c<0.5$) was calculated by means of the all electron self-consistent tight-binding linear muffin-tin orbital (TB-LMTO) method within the atomic-sphere approximation[11] (ASA) combined with the coherent potential approximation[12](CPA). The effects of exchange and correlation were treated within the framework of the LSDA using the parametrization by Vosko *et al.*[13] The integration in reciprocal space has been carried out using 240 and 770 **k** points in the irreducible part of bcc and fcc Brillouin zone, respectively. This allowed us to determine the minima of the total energy with respect to the volume with an accuracy better than 0.001 bohr, which is sufficient to calculate the spontaneous volume magnetostriction ω_s at an accuracy better than 10^{-3}. ω_s is defined in terms of the ratio of the equilibrium volumes in the ferromagnetic FM and the paramagnetic DLM state

$$\omega_s = \frac{V(\mathrm{FM}) - V(\mathrm{DLM})}{V(\mathrm{DLM})}. \tag{1}$$

For the alloys considered the volume magnetostriction in the Invar region is of the order of 10^{-2} rapidly changing to very low values around 10^{-4} outside the Invar regime.[8] The idea of the DLM formalism is to represent magnetic disorder within the CPA by treating a binary Fe_cPt_{1-c} (the same holds for Fe-Pd) alloys as a pseudoternary alloy $Fe^+_{c-x}Fe^-_xPt_{1-c}$ where $c-x$ is the concentration of Fe atoms with up-spin Fe^+ and x of those with down-spin Fe^-. $x=0$ describes a ferromagnetic state, while $x=c/2$ describes a state with spin-up and spin-down local moments equipartitionally distributed on the Fe sites, thus modeling a paramagnetic state of a magnetic alloy. In the ferromagnetic states there exists also a small moment on Pt(Pd) which is induced by the large Fe moments and which disappears in the DLM state independently whether we introduce DLM also on Pt sites or not. In Fe-Co alloys, however, Co sites have a large genuine mo-

ment, therefore to model a paramagnetic state we calculate a four-component alloy $Fe^{+}_{c-x}Fe^{-}_{x}Co^{+}_{1-c-y}Co^{-}_{y}$, with $x=c/2$ and $y=(1-c)/2$.

The experimental estimation of the spontaneous volume magnetostriction is not a straightforward procedure and is plagued with quite some uncertainty.[8] However, it has been pointed out that in Invar alloys ω_s is large and positive as compared to other magnetic materials[8] and that this large value of ω_s is the prototypical anomaly for Invar alloys. Thus any model to explain the Invar problem should give an answer to the origin of this large spontaneous volume magnetostriction[9] and at the same time explain the large variation of ω_s with chemical composition.

Determinations of ω_s for fcc Fe-Pt(Pd) from experiment suggest that ω_s has its maximum value for a chemical composition close to the borderline between the bcc and fcc phase (for $Fe_{75}Pt_{25}$ the values are given by Wassermann:[8] $\omega_s \approx 1.7-1.8\times 10^{-2}$; and by Shiga:[9] $\omega_s \approx 1.5-1.6\times 10^{-2}$). From thereon ω_s decreases almost linearly with increasing valence electron concentration (e/a) due to Pt substitution.[9] At electron concentrations around $(9.0-9.2)e/a$, ω_s becomes small dropping to values below 1.0×10^{-3}. A similar behavior is found for Fe-Pd alloys, with values of ω_s reported to be only slightly smaller. Recently it has been found[14] that bcc $Fe_{1-c}Co_c$ alloys show large positive values of ω_s being of the order of $1-2\times 10^{-2}$ for Co concentrations $0.17<c<0.6$ while pure bcc Fe again has a value of about 10^{-3}.

In Fig. 1 (upper panel) we present the results of our calculations for ω_s as defined by Eq. (1) for disordered bcc Fe-Co and fcc Fe-Pt(Pd) alloys.

The calculated values of ω_s are plotted as a function of the valence electron concentration e/a as in most reviews on the Invar problem. It can be seen that our results fairly well describe the experimental situation found for these alloys. The calculated ω_s in Fe-Pt and Fe-Pd increases with increasing Fe concentration up to the fcc-bcc martensitic phase boundary. With increasing Pt(Pd) concentration, ω_s rapidly drops to low values becoming smaller than 10^{-3} at $e/a \approx 9.1-9.2$. The quantitative comparison with the experimental results for Fe-Pt(Pd) suggests that around the Invar compositions the calculations overestimate the experimental values only by about 20%. In bcc Fe the value of ω_s is found to be below 10^{-3} but grows rapidly with increasing Co concentration ending up in a flat maximum with values $\omega_s \approx 2.2\times 10^{-2}$ again reproducing nicely the experimental results. The existence of such a maximum of ω_s versus e/a is common for Invar systems[8] and the value e/a at which it occurs has often been called *magic electronic number* since this value of about $8.5e/a$ was found to be a universal feature for most transition metal Invar alloys.

The behavior of the magnetostriction is linked to the difference between the value of the local magnetic moments of Fe in the FM and paramagnetic DLM state. In Fig. 1 (lower panel) we plot the calculated Fe local moments in both the FM and DLM states. Comparing the two panels of Fig. 1 it can be seen that the more the local Fe moment decreases in the paramagnetic DLM state as compared to the FM state,

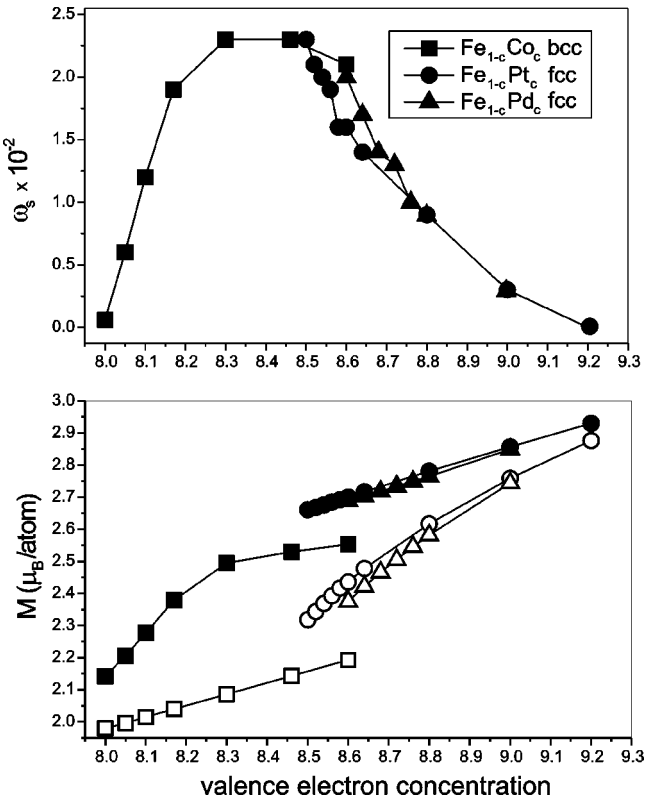

FIG. 1. Calculated volume magnetostriction ω_s (upper panel) and local atomic moments of Fe (lower panel). For the local moments full symbols refer to the ferromagnetic and open symbols to the disordered local moment state, respectively.

the higher the value of the spontaneous volume magnetostriction is, for the respective alloy. The magnetic state of Pt(Pd) plays a minor role for the magnetostrictive properties. Pt(Pd) lose their induced small moments in the paramagnetic DLM state but this does not affect the magnitude of the magnetostriction. This is in contrast to Fe-Co where Co has a significant local-moment change, thus contributing to ω_s as well. The observation that the spontaneous volume magnetostriction scales with the moment change between the FM and DLM state is quite in line with the general observation that a state with higher magnetic moment has a larger equilibrium volume than a state with lower moment, an effect which is usually embodied in what is called magneto-volume coupling. In terms of the electronic band structure this behavior can be explained from the gain in kinetic energy of the valence electrons due to band splitting. This increased kinetic energy becomes partly counterbalanced by an increase in volume. Since the volume changes are thus proportional to the magnetic moment, a strong change in the moments between the FM and the DLM state must also result in a fairly large change of the volume. From electronic structure arguments,[15] which are based on the virial theorem one would expect that the magneto-volume coupling scales, in the lowest order, linearly with the square of the magnetic moment. In Fig. 2 we plot ω_s for all three systems investigated as a function of the difference of the average local moments $M^2(\mathrm{FM})-M^2(\mathrm{DLM})$ and obtain straight lines over the whole concentration range. This result tells us that

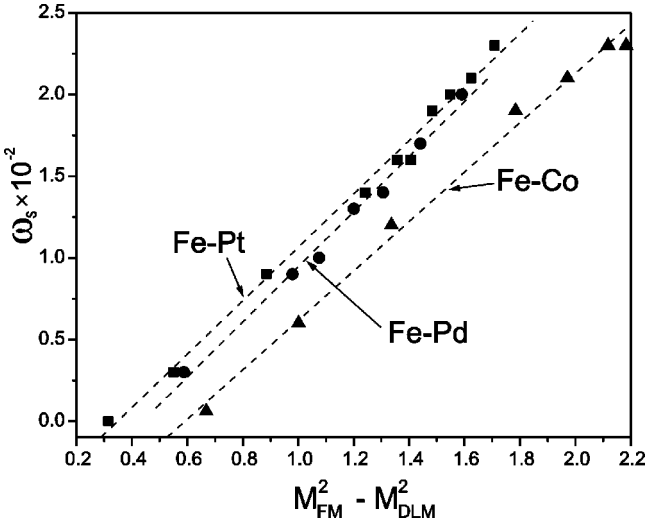

FIG. 2. Linear dependence of ω_s on the difference of the local-moment squared. The dashed lines are respective least square fits and should be guides to the eye.

the magnetovolume coupling constant is essentially unchanged over the concentration range investigated. Only when the changes in the local moments become large does the volume magnetostriction become large as well. The question which finally arises (and thus the explanation of the Invar effect), namely, why some alloys show an anomalously large ω_s, can be traced back to why in Invar alloys the local-moment changes become a maximum as compared to the non-Invar systems. In order to understand these changes of the local magnetic moments, we need to inspect the calculated local atomic density of state (DOS). We begin by discussing pure bcc Fe, which has a small ω_s. Its spin-polarized DOS [Fig. 3(a)] shows the well-known feature that the majority *d* band is not fully occupied leaving space for 0.2–0.3 electrons. Pure bcc Fe is a weak (unsaturated) ferromagnet as compared to pure Ni and Co, which are strong ferromagnets with a fully occupied majority band. In the DLM state significant changes in the DOS of the majority and minority bands (open circles) occur coming from the effects of magnetic-moment disorder, which broaden the peaks of the DOS and make it much smoother throughout. Substituting Co for Fe increases the valence electron concentration and significantly changes the situation. The position of the Fermi level approaches the top of the majority *d* band causing Fe to gradually become a strong ferromagnet. In Fig. 3(b) the local DOS of Fe for $Fe_{70}Co_{30}$ is shown. This alloy shows large value of ω_s close to the maximum (Fig. 1). It can be seen that in the ferromagnetic ground state E_F is almost exactly at the top of the majority $3d$ band, which also means that for this concentration the average FM moment becomes a maximum. In the DLM state the changes of the DOS due to additional magnetic disorder lead to a transition from strong to weak magnetism causing a change of the local Fe moment of $\Delta M = 0.41\ \mu_B$/Fe. The same situation occurs at the Co sites [Fig. 3(c)], where the local moment change is even larger: $\Delta M = 0.85\ \mu_B$/Co resulting in a significant magnetovolume effect. In Fig. 3(d) we present the local DOS of Fe in fcc $Fe_{70}Pt_{30}$ Invar alloy. Again we find that $Fe_{70}Pt_{30}$

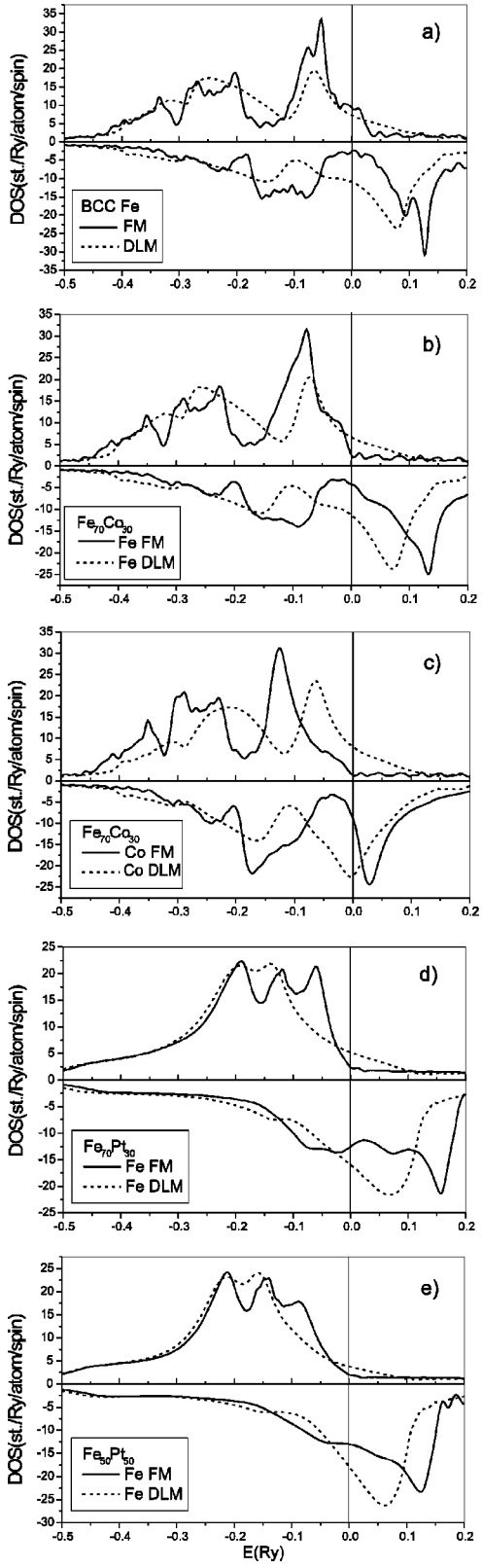

FIG. 3. Atom projected densities of states for the systems investigated. Ferromagnetic state (full line), DLM state (dashed line). For the DOS of the Invar compositions [panels (b), (c), (d)], the Fermi energy is found right on top of the majority *d* band. Positive and negative values of the DOS refer to majority and minority spin, respectively.

is a strong ferromagnet with E_F near the very edge of the majority band and thus shows pronounced Invar behavior. $Fe_{50}Pt_{50}$ [Fig. 3(e)] is a fully developed strong ferromagnet with local moments already lower than for $Fe_{70}Pt_{30}$. This results in much smaller reduction of the local Fe moment ($\Delta M = 0.1\ \mu_B$/Fe) and thus in a lower value of spontaneous volume magnetostriction. Further increase of the Pt concentration will leads to a complete disappearance of the Invar type anomaly. Exactly the same situation occurs in Fe-Pd.

For all cases investigated we find the same effects, which are responsible for the local-moment reduction in the paramagnetic state. They are caused by the dynamical changes of the electronic structure due to magnetic disorder. The moment reduction becomes large when in the FM ground state, the Fermi level is right at the upper edge of the majority $3d$ band and thus the FM local moment is maximal. If upon alloying E_F moves either inside of the 3d majority spin band or is shifted to even higher energies, the subsequent local-moment changes are reduced. This observation gives a strong hint on the reason of the magic electronic number e/a, which for ferromagnetic Invar alloys is found at a valence electron concentration of about 8.5 electrons/atom. At this concentration the Fermi energy just reaches the top of the majority d band causing a transition from weak to strong ferromagnetism. It is striking to note that the maximum of the Slater-Pauling curve is just at $e/a = 8.5$ also marking the transition from weak to strong ferromagnetism. Since the discovery of the Invar effect,[16] a large number of often even controversial theories have been formulated to explain this property. All these theories were linked to peculiarities of single Invar alloys like high-spin and low-spin states,[17] noncollinear magnetic ordering,[18] partial chemical ordering,[19] intrinsic meta-magnetism,[20] etc. We want to point out that features like noncollinear magnetic ordering and partial chemical ordering are characteristic for Fe-Ni Invar alloys and cause additional difficulties for the analysis of the magneto-volume effect. These problems may have been also the reason, why applications of the DLM model to Fe-Ni (Ref. 21) did not lead to definite conclusions about its Invar properties. The mechanism presented here is much more general since it does not depend on these peculiar properties but relies solely on magnetic disorder. We would like to note here that also for the complicated case of Fe-Ni alloys the Invar effect was linked entirely to the changes of the local on-site magnetic moments in the phenomenological single-site spin-fluctuations theory by Kakehashi.[15] Magnetic disorder and its effects on the electronic structure determine the changes of the local moments, which themselves cause the volume magnetostriction. For the Invar compositions ($e/a \approx 8.5$) the local moment changes and the magnetostriction becomes maximal, explaining the occurrence of the thermal expansion anomaly in transition metal Invar alloys in a natural way.

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