Large Negative Magnetic Contribution to the Thermal Expansion in Iron-Platinum Alloys: Quantitative Theory of the Invar Effect

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We show that the large negative magnetic contribution to the thermal expansion in disordered Fe-Pt alloys can be understood within the disordered local moment (DLM) approach. On the basis of first principles calculations we quantitatively describe the spontaneous volume magnetostriction for various Pt concentrations. It is found that the Invar effect in these alloys is entirely related to the state of thermal magnetic disorder modeled by the DLM states. We also show that the experimentally observed anomaly in the temperature dependence of the magnetization is due to a spontaneous reduction of the local magnetic moments rather than to "hidden excitations."

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The understanding of the Invar anomaly found in some magnetic transition metal alloys, such as Fe-Pt and Fe-Ni, has remained a challenging problem of solid state physics for more than 100 years [1]. The main property of Invar alloys is an almost vanishing thermal expansion below the magnetic ordering temperature. It was recognized very early that there must exist a negative contribution to the thermal expansion, which is related to magnetism and which compensates the ever present positive contribution coming from the anharmonicity of the lattice vibrations [2]. The main aim of Invar research is thus to explore the mechanism leading to this negative contribution. A further anomaly which is typical for Invar alloys is the much stronger than usual drop in the magnetization upon increasing temperature [3]. This anomaly has been blamed on the existence of mysterious "hidden excitations," which, however, have never been detected experimentally. Since the discovery of the Invar effect a huge amount of empirical material has been collected [2,4]. The property to keep the volume fairly constant over a reasonable temperature interval makes the technological importance of Invar alloys self-evident [5]. Recent progress in the understanding of the microscopic mechanism underlying the Invar effect is based on the employment of advanced electronic structure calculations. Fixed spin moment calculations for Fe-Ni- [6–8] and Fe-Pt-Invar alloys [9] at first revived the early phenomenological 2γ-state model [10] by providing evidence for the existence of low-spin/low-volume and high-spin/high-volume states. However, such a model does not describe the low temperature behavior properly and would actually require the existence of magnetic inhomogeneities, which have never been confirmed experimentally. A major step towards the understanding was made by applying the disordered local moment (DLM) formalism to Fe-Ni [11,12]. The advantage of the DLM formalism is that it can directly be related to a finite temperature state of the magnetic alloy. For weakly itinerant Fe-Ni Invar such investigations were questioned by van Schilfgaarde *et al.* [13] since they found a volume dependent noncollinear spin alignment which was missing in the earlier DLM calculations. It should be mentioned that earlier supercell calculations also found a noncollinear ground state in $Fe_{35}Ni_{65}$ [14]. In contrast to all previous results, their introduction of noncollinear spin ordering allowed for a continuous magnetic transition, although neutron polarization analysis experiments [15] did not provide any evidence for noncollinearity. From these investigations it can be seen that the case of the Fe-Ni is perhaps the most complicated type of Invar alloy, since it represents a weak itinerant ferromagnet and contains two genuinely magnetic constituents. In contrast Fe-Pt-Invar alloys are strong ferromagnets [2] which exhibit localized magnetic moments residing on the Fe sites. A calculation for ordered Fe_3Pt by Uhl *et al.* [16] yielded a ferromagnetic ground state and a spin-spiral state only at reduced volume. For disordered Fe-Pt there is no experimental as well as theoretical evidence of a possible noncollinear spin structure.

In this Letter we report *ab initio* calculations for disordered fcc-Fe-Pt alloys for varying Pt concentration, applying the DLM formalism which is ideally suited to describe strong ferromagnets with localized magnetic moments. This allows us to quantitatively predict the negative magnetic contribution to the volume expansion causing the Invar anomaly. In addition we find that the stronger than usual drop in the magnetization is due to a spontaneous reduction of the local magnetic moments, so that a hypothesis of hidden excitations becomes unnecessary.

Our investigations are based on the application of the coherent potential approximation (CPA) embodied in a tight-binding linear muffin tin orbital model [17]. In the underlying atomic sphere approximation [18] the size of the Wigner-Seitz radii was set to be equal for all atoms. Disordered systems, such as random substitutional alloys, can be described in terms of an averaging over all possible configurations. The CPA is the effective medium theory

that allows one to calculate averaged Green's functions with high accuracy and is nowadays a standard method in electronic structure theory [19]. Effects of exchange and correlation are treated within the local spin density functional formalism applying the parametrization devised by Vosko *et al.* [20]. The idea of the DLM formalism [21] is to represent magnetic disorder within the CPA by treating a binary Fe_cPt_{1-c} alloy 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^-). The case of $x=0$ describes a ferromagnetic solution, while $x=\frac{c}{2}$ represents a state with spin-up and spin-down local moments equipartitionally distributed on the Fe sites. For local moment systems the latter state models the paramagnetic state above the magnetic ordering temperature T_c. One can thus interpret any partially magnetically disordered state for $0<x<\frac{c}{2}$ as a magnetic state similar to a finite temperature state below T_c. In Fig. 1 we show the result of a minimization of the total energy for the alloy $Fe_{70}Pt_{30}$ for various DLM states which demonstrates a clear shift of the equilibrium volume towards lower values with increasing magnetic disorder. The calculations were performed for 770 k-points in the irreducible wedge of the Brillouin zone, which was found to be sufficient to ensure numerical stability yielding an accuracy of the calculated equilibrium lattice constants better than 10^{-3} bohrs. The calculated spontaneous volume magnetostriction ω_{so}, which is given by the volume reduction between $x=0$ (ferromagnetic state) and $x=35$ (DLM-paramagnetic state) amounts to 1.6%, which is in excellent agreement with the experimental value of 1.4%. Changing the composition to $Fe_{74}Pt_{26}$ yields $\omega_{so}=1.9\%$ which again compares well with experiment giving 1.7% (experimental values are taken from Fig. 23 in Wassermann's review [2]). In order to examine the experimental trend we also performed calculations for $Fe_{50}Pt_{50}$ where the Invar anomaly should be drastically reduced. Our result for ω_{so} is smaller than 0.4% which is no longer sufficient to lead to a pronounced Invar effect in $Fe_{50}Pt_{50}$. In Fig. 2 we collect the results of our calculations for the three alloy concentrations discussed above. Moreover Fig. 2 shows that our DLM approach as well leads to a continuous volume change as a function of magnetic disorder. A major outcome of our investigation is the observed reduction of the local magnetic moment of Fe with increasing DLM concentration for the Fe-Pt Invar compositions. This drop in the local moment can clearly be claimed to be the origin of the deviations found experimentally. This result is in analogy with the findings by van Schilfgaarde *et al.* [13] for Fe-Ni Invar alloys where they also observed, within their supercell approach, that the absolute values of the local moments on Fe and Ni are reduced for noncollinear configurations. Recently it was also found that for the cubic Laves phase Invar compounds $DyCo_2$ and $HoCo_2$ the magnetic moment on Co exhibits a substantial spontaneous reduction induced by the thermal disorder within the rare earth sublattice [22]. Since the observed drops of the magnetic moments in the Invar systems can be explained just from spontaneous changes in the magnetization it can be claimed that there do not exist any hidden excitations whatsoever. It is thus not surprising that any analysis of the temperature dependence of the magnetization which is based on the assumption of constant local moments must inevitably fail.

The continuous changes in the volume and the magnetization which we calculate open the possibility to introduce a relative temperature scale (with respect to T_c) by mapping the partially DLM states to a thermodynamic model of magnetic ordering. To this end, we adopt here a simple molecular field approximation as embodied in the

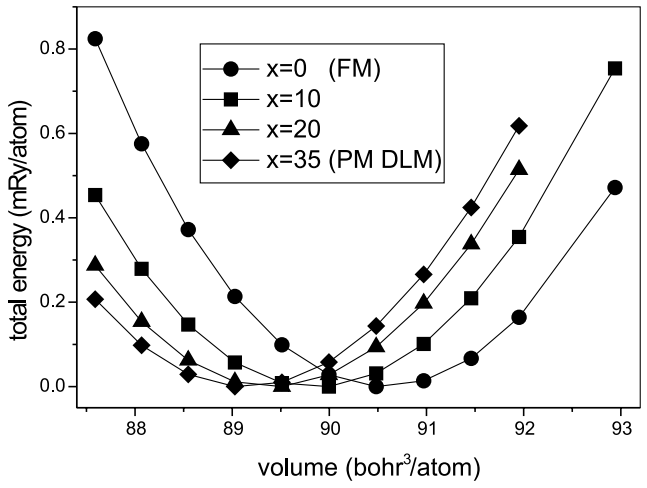

FIG. 1. Total energy versus volume curves for various DLM states of the $Fe^+_{70-x}Fe^-_xPt_{30}$ alloy. The four curves shown are plotted such that their minimum energy is set to zero. Volume and energy is given per atom.

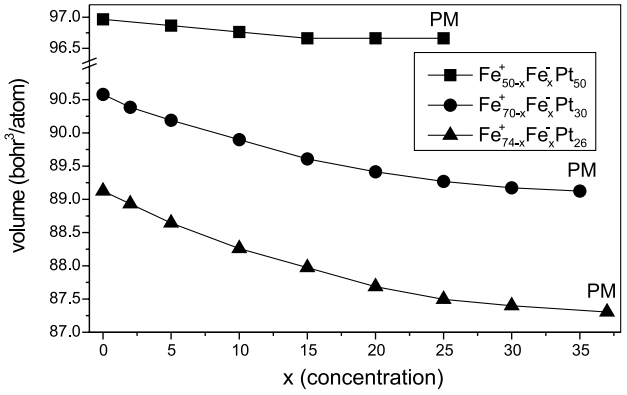

FIG. 2. Dependence of the equilibrium volume on the degree of magnetic disorder x for three chemical compositions. PM stands for "paramagnetism" and denotes the respective DLM state with complete magnetic disorder.

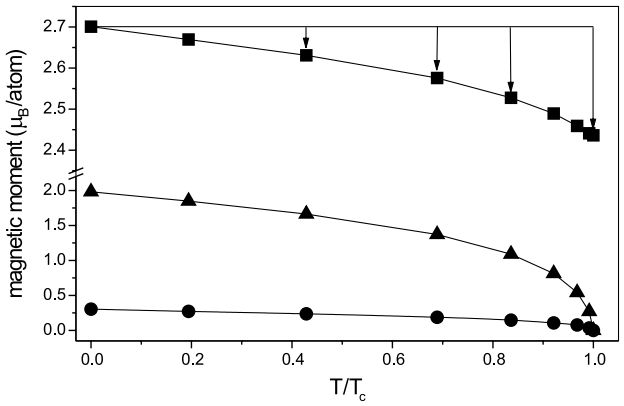

FIG. 3. Temperature dependence of the magnetic moments in $Fe_{70}Pt_{30}$. The average magnetization per atom is given by the triangles; the local moments on Fe and Pt are represented by the squares and circles, respectively. The arrows indicate the spontaneous changes of the Fe local moment M_{loc} with respect to its value at $T = 0$.

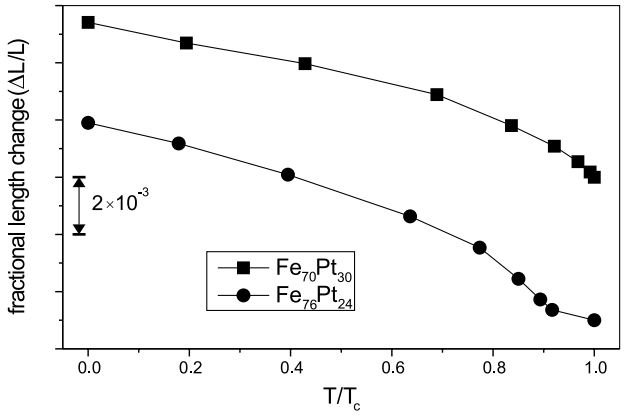

FIG. 4. Fractional length change $\Delta L/L$ as a function of the reduced temperature for two Invar concentrations.

Weiss model [23] but with the modification that the changes in the local moments are accounted for. It should be kept in mind that more refined treatments such as RPA or Monte Carlo simulations based on the classical Heisenberg model may even improve the results. Within the Weiss model the Langevin equation reads

$$M = M_{\mathrm{loc}}\left[\coth\left(\frac{M_{\mathrm{loc}}\Gamma M}{k_B T}\right) - \frac{k_B T}{M_{\mathrm{loc}}\Gamma M}\right], \qquad (1)$$

where M is the average magnetization, M_{loc} is the local atomic moment, and Γ is the Weiss molecular field constant. Our modification is such that M_{loc} is not constant over the whole temperature range but is taken from the actual calculation. With the usual expression for the Curie temperature $T_c = \Gamma M_{\mathrm{loc}}^2/(3k_B)$, where M_{loc} is the value of the Fe local moment for the paramagnetic DLM state, one can introduce a dimensionless temperature scale $t = T/T_c$. Taking M and M_{loc} from our calculations allows one to solve Eq. (1) for t at any given DLM state. Applying this temperature scale we plot the calculated magnetic moments in Fig. 3. It can be seen that there exists also a small moment on Pt which is induced by the large Fe moments at the neighboring Fe atoms and which simply follows the average magnetization thus becoming zero at T_c. The most important observation is made for the local Fe moment M_{loc} which at T_c is reduced by about 10% as compared to its value at $T = 0$ causing the additional magnetization drop observed experimentally. Finally Fig. 4 shows the magnetic contribution to the fractional length changes as a function of temperature in a form which can directly be compared to experiment [24]. It can be seen that the negative magnetic contribution to the thermal expansion is larger for $Fe_{76}Pt_{24}$ than for $Fe_{70}Pt_{30}$ which follows exactly the experimental trend.

We have shown that a full quantitative account of the Invar anomaly in the case of disordered Fe-Pt alloys can be given on the basis of conventional *ab initio* electronic structure calculations employing the disordered local moment approach. Our results not only permit the calculation of the magnetic contribution to the volume changes but also yield a natural explanation for the so-called problem of hidden excitations. It also becomes clearer now why the "classical" Invar alloy Fe-Ni is an even more complex case. The existence of genuine magnetic moments on both the Fe and the Ni atoms [12] and the possible existence of noncollinear magnetic order [13] causes additional complications. One attempt to resolve these difficulties was undertaken by studying chemical short- or long-range order effects, which were found to be important for Fe-Ni but absent for Fe-Pt [12]. However, for the case of disordered Fe-Pt alloys we have shown that only thermal magnetic disorder is required to induce a substantial negative contribution to thermal expansion and thus to explain the observed Invar anomalies.

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