Invar behavior of disordered fcc-Fe_xPt_{1-x} alloys

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Using the tight-binding linearized muffin-tin orbital method combined with the coherent-potential approximation (TB-LMTO-CPA) we have calculated the electronic and magnetic structure of disordered fcc Fe_xPt_{1-x} alloys in a broad concentration range. The total energy was determined as a function of the lattice constant and of the magnetic moment (fixed-spin moment method). For iron concentrations between $x=0.10$ and $x=0.85$ the equilibrium lattice constant, the bulk modulus, and the magnetic moment were determined in good agreement with available experimental data. No deviations of the magnetization from the Slater-Pauling curve in the Invar region were found. In that region two minima of the total energy exist, one with a high moment and a large lattice constant and the other with a zero moment and a small lattice constant, which explains qualitatively the Invar effect. Both minima become degenerate at the critical concentration, $x_c=0.76$. A nonmagnetic ground state was found for $x>x_c$. The energy barrier separating these two minima is two times higher in FePt Invar alloys than in the FeNi system. The relativistic effects were included within the scalar relativistic approximation. [S0163-1829(98)04632-3]

I. INTRODUCTION

The Invar effect has been known as the absence of thermal expansion for a long time.[1] It occurs in several alloys and intermetallic phases; the most famous examples are fcc FeNi and FePt alloys at around 65 to 75% iron. In addition to many similarities there are remarkable differences between both alloys, especially in their magnetic properties. It is known that FeNi alloys show deviations from the Slater-Pauling curve of the magnetic moment in dependence on concentration, $m(x)$, but FePt does not.[1,2] This may be attributed to the difference between weak and strong ferromagnetism, respectively (see Ref. 2 and references therein). In early band theories[3] the Invar effect in FeNi was explained as resulting from the weak ferromagnetic behavior. Such an explanation is, however, not applicable to FePt. More recent, accurate total-energy calculations showed the presence of two nearly degenerate local minima in the total energy $E_{\rm tot}(a,m)$ as a function of the magnetic moment m and the lattice constant a in all the Invar substances considered.[4–8] The deeper minimum has a large magnetic moment and a large lattice constant, whereas the other minimum has zero or a small magnetic moment and a small lattice constant. However, the accurate total-energy calculations yield no deviations from the Slater-Pauling curve in the case of disordered FeNi alloys,[7,8] in contrast to early calculations for FeNi alloys with a fixed lattice constant.[9]

The FePt alloy system has a complex phase diagram with many ordered phases.[10] The stable phase in the Invar region at around 75% iron is the ordered Fe_3Pt intermetallic compound, but disordered alloys can be produced as well, showing also the Invar effect in a narrow concentration range. The two minima of the total energy $E_{\rm tot}(a,m)$ were first established in calculations for ordered Fe_3Ni and Fe_3Pt compounds.[6] For the latter substance also noncollinear effects had been considered.[11] Only recently there appeared calculations that took disorder into account in the case of FeNi alloys[7,8] based on the coherent potential approximation. However, until now, to our knowledge, no calculation of this kind exists for FePt alloys. It is the aim of the present work to fill in this gap. Such a calculation allows one to study the influence of disorder on the total-energy results, but it also has the advantage that the composition of the alloy can be varied, which is not possible for ordered phases. We present the results of the fixed spin moment calculations for disordered fcc FePt alloys and discuss the differences to FeNi.

In contrast to the FeNi system, one expects considerable relativistic effects in FePt alloys due to the large atomic number of Pt. We choose here the scalar relativistic approximation and show the difference from a nonrelativistic treatment, which is especially remarkable for the lattice constant. The paper is organized as follows: the method of calculation is described in Sec. II, the total-energy calculations are presented in Sec. III, and the results are discussed in Sec. IV.

II. THE TB-LMTO-CPA METHOD

The calculations were done using the coherent potential approximation (CPA) formulated within the tight-binding version of the linear muffin-tin orbitals description (TB-LMTO) of solids (see Refs. 12 and 13, where the method is explained in detail). The charge and spin density are determined in a self-consistent manner. The energy integration along a contour in the complex upper half plane was performed by using a Gaussian quadrature with 10 nodes. The k-space integrals were calculated with 182 k points in the irreducible wedge of the fcc Brillouin zone (BZ), corresponding to 6912 points in the full BZ. The radial Schrödinger equation for the core and valence states was solved using the scalar relativistic approximation for the Dirac

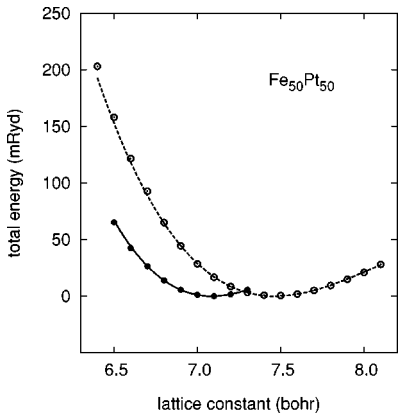

FIG. 1. Nonrelativistic (open circles, dashed line) and scalar relativistic (filled circles, full line) total energy $E_{\mathrm{tot}}(a)$ for $Fe_{0.50}Pt_{0.50}$ as a function of the lattice constant a. The minima of both curves have been set to zero energy, and the lines are due to a polynomial interpolation of the nonmagnetic values.

equation.[14] The relativistic corrections have a considerable effect on the results for Fe_xPt_{1-x} alloys as will be discussed below. The Wigner-Seitz radii of both constituents have been chosen to be equal and according to the atomic sphere approximation (ASA). Consequently, the Wigner-Seitz spheres are not neutral and due to the charge transfer the Madelung potential appears. Its effect was taken into account in terms of the screened-impurity model[15] with a parameter $\beta=1$ corresponding to the assumption of a complete disorder. The exchange and correlation potential of Vosko, Wilk, and Nusair[16] was employed. The total energy was calculated with an accuracy of 10^{-3} mRyd.

The calculations can be carried out in two ways, depending on the treatment of the spin splitting and magnetic moments: (i) the standard procedure in which both the spin splitting and the average alloy magnetic moment are results of the calculation, and (ii) the fixed spin moment (FSM) method[17] in which the magnetic moment is fixed and the spin splitting is determined in the self-consistent calculation, usually by introducing two different Fermi levels for spin-up and for spin-down electrons. The FSM method is more suitable as it allows for direct determination of the total energy $E_{\mathrm{tot}}(a,m)$ as a function of the lattice constant a and of the magnetic moment m, which is needed in studies of a moment-volume instability. Both approaches are equivalent in the sense that for a fixed lattice constant the magnetic moment m_0 calculated by the standard approach is the same as the magnetic moment m_0 for which the FSM total energy $E_{\mathrm{tot}}(a,m_0)$ has its minimum, and $E_{\mathrm{tot}}^{\mathrm{FSM}}(a,m_0)=E_{\mathrm{tot}}^{\mathrm{std}}(a)$.

One difference between Fe_xPt_{1-x} and Fe_xNi_{1-x} alloys is the amount of relativistic effects in the former system. Due to the large atomic number of Pt the corresponding states are contracted in comparison with a nonrelativistic calculation. It is illustrated in Fig. 1, where we compare a nonrelativistic and a scalar relativistic total energy of $Fe_{0.50}Pt_{0.50}$ alloy. The calculations were done for a decreasing series of lattice constants, and the results of the previous calculation were used as an input for the next one. In this way we have achieved that the solution with a high magnetic moment remained stable up to 6.8 or 6.7 Bohr units in the nonrelativistic or scalar relativistic case, respectively. A contraction of the lattice due to the relativistic effects is clearly seen in Fig. 1. Such a strong contraction is not observed in the FeNi system and shows the importance of relativistic effects for FePt alloys.

III. RESULTS OF TOTAL-ENERGY CALCULATIONS

We have performed total-energy calculations for a series of fcc Fe_xPt_{1-x} alloys with $0\leqslant x\leqslant 0.85$, and in the Invar region, we have calculated the FSM energy contours for $x=0.7,0.75$, and 0.8 [Figs. 2(a)–2(c)]. All three energy contours $E_{\mathrm{tot}}(a,m)$ show two energy minima, one with a large magnetic moment and a large lattice constant, and the other with a smaller lattice constant and without magnetic moment. By changing the Fe concentration, the two minima are mutually shifted. At the critical concentration, $x_c\approx 0.76$, both minima have the same energy. For iron-rich alloys, $x>x_c$, the nonmagnetic ground state is stable, but for $x<x_c$ one finds a magnetic solution (except the nonmagnetic pure fcc platinum). The total energies $E_{\mathrm{tot}}(a)$ of the magnetic and of the nonmagnetic solution as functions of the lattice constant are shown in Fig. 3 for the $Fe_{0.75}Pt_{0.25}$ alloy. This alloy belongs to the Invar region and it has two nearly degenerate minima, the energy of the magnetic solution being lower only by 0.7 mRyd. In a certain range of lattice parameters (between 6.775 and 7.0 atomic units) both solutions are locally stable and can be calculated by changing the lattice constant inwards or outwards, respectively.

These two minima explain the Invar effect of fcc Fe_xPt_{1-x} alloys around $x=0.75$ at least qualitatively in the sense as it was first discussed by Weiss.[18] The effect occurs for a magnetic alloy for which the nonmagnetic minimum with a small lattice constant (or a minimum with a small moment) is only slightly above the magnetic solution with a large lattice constant. By increasing the temperature the local minimum with small lattice constant can be populated by thermal fluctuations, which counteracts the usual thermal expansion due to lattice vibrations. In fact, already a close neighborhood of the magnetic minimum will be disturbed by the second, nearly degenerate solution such that the absolute value of the third derivative d^3E_{tot}/da^3 at the minimum becomes smaller. That gives rise to a small value of the Grüneisen constant γ according to the formula[19]

$$\gamma=-1-\frac{a_0}{6}\left.\frac{E_{\mathrm{tot}}'''}{E_{\mathrm{tot}}''}\right|_{a_0}.$$

We find Grüneisen constants of 0.58, 0.05, and 0.92 for three iron concentrations $x=0.70,0.75$, and 0.80 for which the energy contours are shown in Figs. 2(a)–2(c), respectively.

For comparison we show in Fig. 2(d) also the energy contour of the $Fe_{0.70}Ni_{0.30}$ Invar alloy. Our result coincides with former calculations.[7,8] Besides the general similarity between both compounds one may observe that the two minima are better separated for FePt Invar alloys than for the FeNi system. Two minima are separated by a barrier of 2.1 mRyd in $Fe_{0.75}Pt_{0.25}$ alloy, while the barrier height in $Fe_{0.70}Ni_{0.30}$ is only 1.1 mRyd.

Besides the Invar region we investigated also fcc Fe_xPt_{1-x} alloys in the whole concentration range. For $x>0.85$ the fcc phase is clearly unstable experimentally and

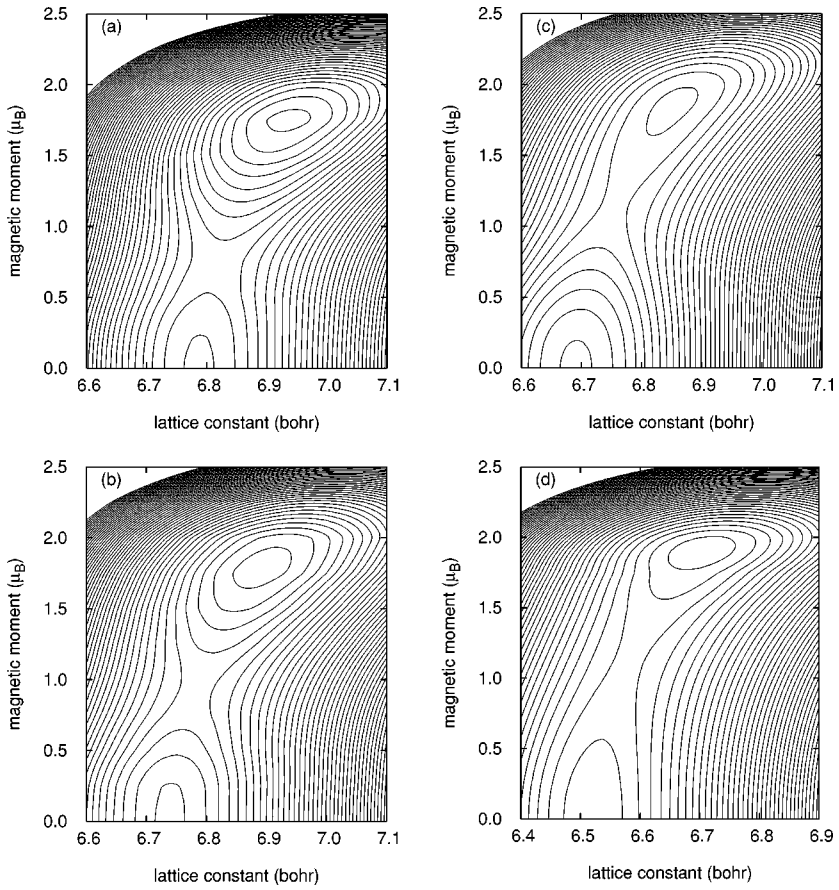

FIG. 2. Contour plots of $E_{tot}(a,m)$ for (a) $Fe_{0.70}Pt_{0.30}$, (b) $Fe_{0.75}Pt_{0.25}$, (c) $Fe_{0.80}Pt_{0.20}$, and (d) $Fe_{0.70}Ni_{0.30}$. The energy difference between neighboring isolines is 0.5 mRyd.

we carried out no calculation. For concentrations up to 75 at. % of iron we find a magnetic solution. With the help of polynomial interpolation, we can calculate the equilibrium value of the lattice constant a_0, the bulk modulus B, and the magnetic moment m, which are given in Table I. For the two concentrations, $x=0.8$ and 0.85, the nonmagnetic curve is the lower one. This leads to a discontinuity in the dependence of bulk modulus and lattice constant on concentration.

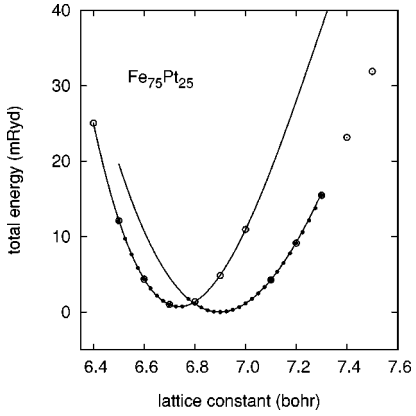

FIG. 3. Total energy $E_{tot}(a)$ of high-moment and zero-moment solutions for $Fe_{0.75}Pt_{0.25}$. The different solutions have been found by changing the lattice constant inwards (filled circles) or outwards (big open circles), respectively. The absolute minimum of the energy has been set to zero, and the lines result from polynomial interpolation.

IV. DISCUSSION AND CONCLUSION

Let us first compare the theoretical results (Table I) with available experimental data. In general, the coincidence is not bad. The theoretical lattice constants in the Invar region are slightly smaller than the experimental ones. Note, however, that for pure Pt our calculation gives a slightly larger

TABLE I. Lattice constant a_0 in atomic units (a.u.) and in Å (in parentheses), bulk modulus B, and magnetization m of disordered fcc Fe_xPt_{1-x} alloys at several iron concentrations x.

	a_0/a.u.(a_0/Å)		B/Mbar		m/μ_{Bohr}	
x	Theory	Expt. [a]	Theory	Expt. [b]	Theory	Expt. [b]
0.00	7.48 (3.96)	7.41 (3.92)	2.70	2.83	0.00	0.00
0.10	7.41 (3.92)	7.37 (3.90)	2.97		0.49	0.38±0.05
0.20	7.33 (3.88)	7.35 (3.89)	3.05		0.81	0.80±0.05
0.30	7.24 (3.83)	7.31 (3.87)	3.00		1.06	1.02±0.05
0.40	7.16 (3.79)	7.28 (3.85)	2.81		1.28	1.31±0.05
0.50	7.09 (3.75)	7.22 (3.82)	2.64		1.48	1.48±0.05
0.60	7.01 (3.71)	7.16 (3.79)	2.48		1.65	1.75±0.05
0.65	6.97 (3.69)		2.39		1.72	
0.70	6.93 (3.67)	7.11 (3.76)	2.28		1.78	2.00±0.05
0.75	6.90 (3.65)	7.05 (3.73)	2.11	1.95	1.81	2.02±0.05
0.80	6.69 (3.54)		3.36		0.00	
0.85	6.64 (3.51)		3.35		0.00	

[a]From Fig. 92 of Ref. 2.
[b]From Ref. 20.

value than experiment, which is a well-known feature of scalar relativistic calculations[6,19] for heavier elements. The calculated as well as measured magnetic moments increase with iron content according to the Slater-Pauling curve. There are some deviations between experimental and theoretical moments: the theoretical values are too low in the Invar region and too large at small iron concentration. Consequently, at least part of the discrepancies can be ascribed to the deviations in the lattice parameter. Unfortunately, there are only few experimental results for the bulk modulus, but they agree quite well with our calculation. It would be interesting if the theoretically predicted maximum of the bulk modulus at around 20 at. % iron could be confirmed experimentally.

The present CPA calculations for FePt agree better with experiment than similar calculations for FeNi.[7,8] The problem with FSM-CPA calculations occurs for FeNi, where the deviations from the Slater-Pauling curve cannot be reproduced. Our calculations confirm those insufficiencies in the FeNi case. We find smaller critical concentration for FeNi (72% iron) than for FePt (76%), a tendency that is known from the experimental data.[1] Our calculations yield higher barrier between two minima for FePt than for FeNi. This fact could explain some differences in the behavior of these two systems.

The present calculations for some compositions (25, 50, and 75 at. % of iron) can be compared with results obtained for ordered phases. [5,6] There is a good agreement for lattice constant, bulk modulus, and magnetization, both between calculations for ordered and disordered phases, and with experimental data. The only exception is the ordered phase $FePt_3$, which is antiferromagnetic, in contrast to the disordered phase, which is ferromagnetic. In the present work we have simply assumed a ferromagnetic spin alignment in agreement with the experimental situation. At Invar composition (Fe_3Pt) the disorder has two effects: (i) the low-spin phase of the ordered Fe_3Pt goes over into a zero-spin phase, and (ii) the energy difference between the high-spin and low-spin (zero-spin) phases diminishes [from 1.2 mRyd (Ref. 6) to 0.7 mRyd].

In conclusion, we have found two energy minima in the Invar region of disordered FePt alloys that are better separated than for FeNi. This could explain at least some differences in the behavior of FePt and FeNi Invar alloys, but it does not explain all of them. One can speculate that a simple ferromagnetic spin alignment assumed in our calculations is not sufficient for a complete answer as it was discussed recently.[11,21]

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