Basic Understanding of the Relations between Invar, Anti-Invar and Martensite in Fe-based Alloys

E.F. Wassermann, M. Acet, P. Entel, and W. Pepperhoff
Experimentelle und Theoretische Tiefen temperaturphysik und SFB 166
Gerhard-Mercator Universität Duisburg, 47058 Duisburg, Germany

(Received; May 18, 1998) Accepted; August 26, 1998)

Based on experimental results of high temperature thermal expansion, paramagnetic neutron scattering, considerations of the relative stability of the various phases of elemental Fe and total energy calculations, we discuss the interrelated aspects of Invar, anti-Invar and martensitic phase transformations in Fe-rich alloys. The physical background to the discussions is provided by ab initio calculations of the magnetic and structural binding surfaces of pure Fe and Fe-based alloys. Decisive are charge transfers between electronic levels with different symmetry (e_g and t_2g) and their non-bonding and anti-bonding character. The variation with composition of the size of the Invar and anti-Invar effects is a question of the position of the Fermi energy relative to these levels. How an effect manifests itself as a function of temperature is a question of the energetic difference between these levels.

**Key words:** itinerant magnetism, transition metal alloys, fcc-iron, magnetovolume effects, Invar effect, anti-Invar effect, martensitic phase transitions

1. Introduction

1.1 Allotropy of pure Fe

The starting point of accounts given in this paper is the discussion of the allotropy of pure Fe, which is shown in the phase diagram in Fig. 1 in a plot of temperature versus pressure. At atmospheric pressure Fe solidifies in the bcc β-phase. Below the A_β point at 1665 K a structural phase transition occurs on cooling, and for T < 1665 K down to 1184 K (the A_γ point) Fe has the fcc structure (γ-Fe). Yet, on further cooling below the A_γ point Fe does not become hcp (ε-Fe) as one would expect from its position in the periodic table (note that the elements Ruthenium and Osmium below Fe in column VIII are hexagonal), but the bcc structure returns (α-Fe), and remains as the stable structure down to 0 K. Thermodynamic considerations show that strong ferromagnetic (FM) exchange is a sufficient condition for the stability of the α-phase. Long range FM ordering, which occurs well below the A_β point at a Curie Temperature T_C = 1040 K, is a necessary condition.

The atomic volume of the high temperature γ-phase of Fe is smaller than that of α-Fe. This can be seen in Fig. 1, where the γ-range broadens under pressure. Only hcp Fe (ε-Fe) occurring under high pressure is denser packed than the γ-phase, as the course of the γ-ε boundary line in Fig. 1 shows. If one extrapolates linearly this boundary to zero pressure (dotted line), one obtains at ~490 K the hypothetical γ-ε transition temperature, in the case that ε-Fe were non-magnetic.

The allotropy of Fe began to be understood from first principles with the development of ab initio band calculations. These calculations simultaneously showed that the magnetic coupling in the ground state of fcc-Fe could be antiferromagnetic (AF) or FM, depending on volume, thereby also corroborating the 2γ-states model proposed by Weiss. In Fig. 2 we show recent results, in a plot of the total energy (bottom panel) and the magnetic moment μ (top panel) versus the atomic volume V_a on bcc, fcc and hcp Fe. One can compare these results with the phase diagram in Fig. 1. Most stable, i.e., lowest in total energy, is the FM bcc ground state with the minimum at V_a = 77.37 a.u.³ (lattice constant a = 2.84 Å), which is about equal to the observed value of V_a = 76.55 a.u.³ (a = 2.83 Å). The corresponding moment changes continuously with volume and has a value of about μ = 2.2 μ_B at the equilibrium volume. Note that if the bcc state were nonmagnetic (NM) the total energy curve (not shown in Fig. 2) would have lied about 35 mRy higher than the bcc state (1 mRy = 150 K), so that NM bcc Fe is not stable. The structure with the next highest energy is hcp, situated about 5 mRy above the bcc ground state. However, the minimum lies ~10 a.u.³ lower in volume so that this state can only be reached under high pressure, in agreement with Fig. 1. The next stable structure in Fig. 2 is AF fcc with μ = 1.5 μ_B at the
Fig. 2 Total energy and magnetic moment versus volume at $T=0$ K of Fe in the bcc, fcc and hcp structures.

Fig. 3 The difference in the Gibbs free energy of the $\alpha$ (bcc), $\gamma$ (fcc) and $\epsilon$ (hcp) phases, showing their relative stabilities. The inset shows the details for temperatures in the vicinity of the $A_1$ and $A_4$ points.

equilibrium volume $V_\alpha=73$ a.u.$^3$ ($a=3.51$ Å). The experimental values are $\mu=0.7 \mu_B$ and $V_\gamma=76.19$ a.u.$^3$ ($a=3.56$ Å). This is the state with the small moment and volume of $\gamma$-Fe in the Weiss model.$^3$ Energetically this state is 7.5 mRy ($\sim 1125$ K) above the bcc ground state; a value almost in quantitative agreement with $A_1=1184$ K in Fig. 1. If the volume of the fcc AF state is enlarged, a FM state lower in energy for $V_\gamma>80$ a.u.$^3$ ($a=3.62$ Å) is favored. This means that above this volume the stable state of $\gamma$-Fe is the FM high spin (HS) state. The magnetic moment of this state is about $2.7 \mu_B$, which is in agreement with the value of $2.8 \mu_B$ expected from the valence electron concentration (e/a) dependence of $\mu$ (Slater-Pauling curve). A low spin (LS) state solution also exists for the FM case, having a minimum near the equilibrium volume of the AF solution with $\mu$ ranging between 0 $\mu_B$ and 1 $\mu_B$, so that $\mu$ in the FM solution changes rapidly from small values to 2.7 $\mu_B$. This is known as the moment-volume instability.

From thermodynamical considerations one can understand the relationship between the stability of the bcc phase and FM exchange. If there were no FM exchange the bcc phase would have not been stable, as is seen in Fig. 3 where the differences between the Gibbs free energies of the $\alpha$, $\gamma$ and $\epsilon$ phases are shown. Such an analysis is made by the use of specific heat data.$^7$ NM in the figure denotes non-magnetic which implies "without any magnetic correlation," both for bcc and fcc Fe. The figure shows that $\alpha$ is stable with respect to $\gamma$, except for $A_1 \leq T < A_4$, as long as $\alpha$ is magnetic. The very small value of $G^{\alpha}\cdot G^\gamma$ for $A_1 \leq T < A_4$ shows that the stability of the $\gamma$ phase can be very sensitive to alloying. It can be broadened or destabilized by introducing the appropriate element, $\epsilon$, compared to $\gamma$, is more stable for about $T \leq 400$ K, in good agreement with the value in Fig. 1. If the anti-Invar contribution of $\gamma$-Fe to the specific heat is disregarded, one finds that $G^\alpha\cdot G^\gamma_{\text{NM}}$ is always negative, which means that without the anti-Invar effect, which provides the HS state with FM exchange, the $\gamma$ phase cannot be stabilized.

1.2 Invar and Anti-Invar in Fe-based Alloys

In our recent experimental reviews$^8$ and theoretical studies$^9$ the present understanding of magnetovolume effects and magnetic phase transitions of Fe-based alloys has been discussed in detail, so that we summarize here the basic observations. Typical for Invar is the volume increase in the magnetically ordered range, which leads, relative to a non-magnetic lattice curve (Grüneisen curve), to a reduced thermal expansion below the magnetic ordering temperatures. In ferromagnetically ordered systems this is called the FM Invar effect and in antiferromagnetically ordered systems it is known as the AF Invar effect. Figure 4 shows the results of our thermal expansion measurements on FM fcc Fe$_{28}$Ni$_{72}$ Invar, Fe$_{50}$V$_{50}$Cr$_{15}$ and AF Fe$_{80}$Ti$_{14}$ with a hexagonal C14 Laves phase structure. $\alpha$ is the thermal expansion coefficient. Note that in all alloys the FM or AF Invar effect vanishes above the magnetic ordering temperatures and thus, the reference curve ($\alpha_{\text{cubic}}$) can be obtained by a Grüneisen analysis. The area between the lattice curve and the experimental data gives the volume enhancement due to the Invar effect and corresponds to the
volume magnetostriction at zero temperature $\omega_m^o$. This value is maximum for the FM Invar Fe$_{50}$Ni$_{50}$ (e/a=8.7) with $\omega_m^o = 1.6\%$. For AF Invar the maximum value is $\omega_m^o \sim 0.9\%$ for the Fe$_{50}$Mn$_{50}$ alloy with e/a=7.4.

Anti-Invar is the opposite of Invar behavior and denotes the increase of volume and the enhancement of the thermal expansion relative to a non-magnetic reference. Anti-Invar is observed in $\gamma$-Fe and fcc Fe-rich systems in the high temperature paramagnetic range. The volume increase due to the anti-Invar effect can be determined quantitatively by plotting $\alpha T_m = f(T/T_m)$, where $T_m$ is the melting temperature. For "normal" metals and alloys such a plot results in an almost universal expansion curve. We use this curve as a Gr"uneisen-like reference for the thermal expansion of the alloys in question. Figure 5 shows such a plot for alloys of the Fe$_{100-x}$Ni$_x$ system in the fcc stability range together with the data for pure $\gamma$-Fe above the A$_1$ point. The alloys with $x = 78$ at.\% and 82 at.\% are taken from Ref. 20. Relative to the average lattice expansion curve $\alpha_{LMT} = f(T/T_m)$ the curve for the Invar alloy Fe$_{50}$Ni$_{50}$ deviates below $T_m$ to smaller values. In Fe$_{50}$Ni$_{50}$ a continuous transition from FM Invar at low temperatures to anti-Invar behavior at high temperatures is observed, since there is now also a deviation from the reference curve to larger values (enhancement) above $T_m/T_m$. For $x \geq 75$ at.\% one encounters only anti-Invar behavior. Analogous transitions from Invar to anti-Invar behavior with increasing Fe concentration as in Fig. 5 have also been found in Fe-rich Fe-Pt and Fe-Ni-Co alloys. On decreasing temperature the anti-Invar behavior terminates at the martensite start temperatures $M_s$, where a transition to the bcc (or bct) martensitic phase takes place.

2. Microscopic understanding of Invar and Anti-Invar

Deeper insight into the microscopic background of the Invar and anti-Invar effects is gained from calculations resolving the properties of the d-orbitals with $t_{2g}$ and $e_g$ symmetry. The $t_{2g}$ orbitals have a maximum charge density in the [110] direction and thus in an fcc lattice form strong d$d\sigma$ bonds with nearest neighbors. The $t_{2g}$ density of states (DOS) is split and shows an energetically highly lying peak with antibonding (AB) character and an energetically low-lying one with bonding (B) character. The $e_g$ orbitals have maximum charge densities in the [100] direction and therefore, in an fcc lattice form d$d\pi$ bonds with the nearest neighbors. They are non-bonding (NB) and, in the fcc DOS, are found between the two $t_{2g}$ peaks. The position of the Fermi energy $E_F$ relative to these levels, which depends on the electron concentration e/a, atomic volume and the temperature, determines which type of transition between these levels occur, to lead to the Invar or anti-Invar effects or to a martensitic transformation.

The physical properties of magnetovolume effects and martensitic transitions in Fe-based alloys can be discussed with the aid of ground state properties determined from \textit{ab initio} band calculations. A simplified picture is given in Fig. 6. The upper part of the figure (a to f) shows, for anti-Invar and Invar, the volume dependence of the total energy,

---

Fig. 4 $\alpha$ vs. $T$ of Fe$_{50}$Ni$_{50}$ (fcc, FM), Fe$_{50}$C (cementite, FM) and Fe$_{50}$Ti$_{50}$ (C14 Laves phase, AF).

Fig. 5 $\alpha T_m$ vs $T_m$ for Fe-rich Fe-Ni alloys. The curves for 70 at.\% $\leq x \leq 100$ at.\% are measured down to their corresponding $M_s$ Temperatures.
magnetic moment and the $c_{e}$ and $t_{2g}$ occupation. $V_{e}$ denotes the equilibrium volume and $V_{c}$ the critical volume where the equilibrium state becomes energetically unfavorable. The lower part of the figure (g to j) shows the DOS diagrams. Figure 6a shows that in anti-Invar the LS state is of lowest energy at an equilibrium volume $V_{0}$ and a HS state is present at $V > V_{c}$, where $V_{c}$ is the critical volume above which the HS state is of lower energy. The presence of the HS state causes an enhanced anharmonicity of the lattice. The right hand panel (Fig. 6b) of the total energy, typical for Invar, has the opposite type of enhancement in the anharmonicity in $E(V)$, namely one towards smaller volumes. Here the LS state is at $V < V_{c}$. Calculations show that with increasing e/a anti-Invar behavior progressively transforms to Invar behavior, as $\Delta E$ decreases, goes through zero (so that LS and HS states are practically degenerate) and then increases again with the HS state becoming lower in energy. The key point is that in Invar as well as in anti-Invar the energetic differences between the HS and the LS states is in the order of several mRy. Because of the smallness of the energy differences, transitions from the ground state to the energetically elevated state are possible by raising the temperature. The effect of raising the temperature is shown with the arrows. In anti-Invar LS–HS transitions occur, in which case the magnetic moment increases (Fig. 6c), and in Invar HS–LS transitions occur and the magnetic moment decreases (Fig. 6d). The temperature increase causes, in anti-Invar, the occupation of strongly repulsive AB states to increase sharply at the expense of NB states, leading to an enhanced expansion (Fig. 6e). In Invar, on the other hand the AB states are depopulated so that the volume shrinks (Fig. 6f).

The DOS of anti-Invar in the LS and HS states is schematically shown in Fig. 6g and 6h respectively. (For brevity, the LS DOS of anti-Invar and Invar are shown to be non-magnetic.) In the ground state (LS) of anti-Invar (Fig. 6g) the Fermi energy lies just above the NB $e_{g}$ peak and slightly below the large $t_{2g}$ peak, which is empty. On an increase of temperature the charge transfer from NB $e_{g} -$ AB $t_{2g}$ leads to a spin splitting, and, because of the AB character of the $t_{2g}$ majority state, to an enhanced increase of the volume. The final situation in the DOS looks like that shown in Fig. 6h.

In Invar the case is reversed (Fig. 6i and 6j). $E_{F}$ lies just above the large majority $t_{2g}$ peak and close to a deep valley in the minority $e_{g}$ DOS. The calculations also reveal that in Fe-Ni Invar, in a certain direction of the Brillouin zone, majority spin bands with $t_{2g}$ symmetry and AB character cross with a minority $e_{g}$ band with NB character right at the Fermi energy $E_{F}$. At the volume where the transition from the HS to the LS state occurs, there is a charge transfer, and the $t_{2g}$ majority level is depopulated at the expense of the $e_{g}$ minority level. This means that in the LS state the DOS looks like that shown in Fig. 6j. The transitions from the AB $t_{2g}$ to the NB $e_{g}$ level cause the volume to shrink, thus counterbalancing the normal thermal expansion arising from multi-phonon scattering. This is the physical background of the Invar effect. We should note that the scenario described is not identical to the original two states model of Weiss accounting for HS-LS transitions as single particle excitations on a specific localized.

Fig. 6 The schematic volume dependence of a,b) the total energy, c,d) the magnetic moment, e,f) occupation of orbitals of Invar and Anti-Invar. DOS of g,h) antiInvar and i,j) Invar are shown in the bottom panel. Arrows indicate the direction of response of the system to increasing temperature.
atom. Here we deal, however, with collective excitations, called moment-volume fluctuations.

3. The Paramagnetic Response of Invar and Anti-Invar

Neutron diffraction with polarization analysis gives the capability of investigating the magnetic interactions in the paramagnetic state and, therefore, is an ideal method for investigating the properties of anti-Invar at high temperatures. Experiments on polycrystalline samples of fcc Fe$_x$Ni$_{100-x}$ with $0 \leq x \leq 100$ at. % in the wave vector range $0.15 \AA^{-1} \leq q \leq 2.5 \AA^{-1}$ yield only forward scattering in the magnetic cross section indicating that the magnetic correlations are FM in nature.$^{22,23}$ No AF correlations have been observed in the experiments, although the ground state of these alloys are expected to be AF with $T_N \leq 60$ K.$^{22}$ The temperature dependence of the observed magnetic moment $\mu_{obs}$, which is calculated by integrating the magnetic cross section over the first Brillouin zone$^{24}$, is given in Fig. 7. Data from other literature for fcc Fe and Ni are also included in the data.$^{24,25}$ In this figure two distinct features, one in the temperature dependence of $\mu_{obs}$ and the other in its concentration dependence, are found to be remarkable.

- $\mu_{obs}$ of Fe$_x$Ni$_{100-x}$ for $65 \leq x \leq 100$ at. % increase with decreasing temperature and their behavior conform to a mean field behavior in agreement with earlier results.$^{24}$ However, for higher Fe concentrations the temperature dependence weakens and eventually $\mu_{obs}$ becomes practically temperature insensitive for $x=85$ at. %. For $x=90$ at. % the temperature behavior reverses and $\mu$ increases weakly with temperature. For fcc Fe the temperature variation is nearly constant.

- From the Slater-Pauling curve fcc Fe in the FM state is expected to have $\mu \sim 2.8 \mu_B$ and $\mu$ is expected to decrease with increasing Ni concentration. However, Fig. 7 shows that $\mu_{obs}$ of fcc-Fe is not only far from this value with $\mu_{obs} \sim 1 \mu_B$, but $\mu_{obs}$ also increases with increasing Ni concentration for $100 \geq x \geq 55$ at. % at all temperatures. These unusual properties are discussed in relation to ground state properties in section 4.

4. Discussion

4.1 Finite temperature properties related to ground state properties

With the aid of the ground state properties discussed in section 1.2, it is possible to understand the behavior of the observed magnetic moment $\mu_{obs}$ in Fig. 7. The absence of AF correlations is due to the fact that the fcc stability ranges of the alloys lie well beyond $60$ K, which is around the maximum possible $T_N$ of the Fe-Ni series.$^{24,25}$ Therefore, for a discussion concerning high temperature properties the AF branch in Fig. 2 is neglected and one accounts for the effects by using the presence of the LS and HS states within the FM solution, as in Fig. 6.

The behavior of the temperature dependence of $\mu_{obs}$ results from a superposition of two effects. The first contribution comes from the normal decrease of the magnetic moment with increasing temperature according to a mean field behavior ($\mu_{mf}$), which also governs the temperature behavior of the susceptibility. The second is the contribution from thermally induced LS - HS transitions ($\mu_{LS-HS}$). In anti-Invar the HS state is progressively accessed as the temperature is increased leading to an increasing contribution of the HS moment to $\mu_{obs}$ so that at any temperature

$$\mu_{obs}(T) = \mu_{mf}(T) + \mu_{LS-HS}(T).$$

Depending on which contribution is dominant $\mu_{obs}$ can decrease, remain constant, or even increase with increasing temperature. As we have shown in Fig. 5, $\alpha(T)$ of Fe$_{24}$Ni$_{76}$ (and Ni; not shown) at high temperatures conform to a Grüneisen behavior and are not anti-Invar. Therefore, in this case the mean field behavior of the magnetic moment alone accounts for the temperature dependence of $\mu_{obs}$ of alloys with higher Fe concentrations, which are anti-Invar, begin to deviate from mean field behavior as the contribution from LS - HS transitions become effective and eventually become dominant enough to render $\mu_{obs}$ temperature insensitive.

The second unusual property observed in the experiments is the fact that the $\mu(T)$ curves lie at larger values with increasing Ni concentration. There are two contributions to the concentration dependence of $\mu_{obs}$ at finite temperature. The first is the filling of the d-band with increasing Ni concentration that tends to decrease $\mu_{obs}$ according to the properties given by the Slater-Pauling curve (SP) and the second is the decrease of $\Delta E$ as Ni is added to Fe. In anti-Invar a small $\Delta E$ provides the HS state to be more readily accessed than a larger $\Delta E$ and therefore, causes the LS - HS transition to contribute increasingly to $\mu_{obs}$ as the Ni
concentration increases. The relationship can be written as

\[ \mu_{\text{obs}}(c) = \mu_{\text{sp}}(c) + \mu_{\text{LS-HS}}(c), \]  

(2)

where \( c \) is the concentration. When the \( x=65 \) at.\% Invar concentration is reached the anti-Invar effect disappears and there are no longer contributions to \( \mu_{\text{obs}} \) from LS-HS transitions. However, \( \mu_{\text{obs}} \) continues to increase up to \( x=55 \) at.\%, but this time in accordance with the conventional weak to strong ferromagnetism transition, seen as the deviation from the Slater-Pauling curve. For \( x=55 \) at.\% \( \mu_{\text{obs}} \) decreases with increasing Ni concentration as the d-band fills.

These results so far provide the most direct evidence for the reversal of the ground state from LS to HS as one moves from anti-Invar to Invar, and for the occurrence of LS-HS transitions as the temperature is increased. Paramagnetic scattering experiments under pressure within the fcc stability range are required to observe directly a volume dependence of the magnetic moment at finite temperatures.

4.2 Anti-Invar and the martensitic transformation

The presence of the anti-Invar effect in the fcc stability range of Fe-rich alloys raises the question of what role the anti-Invar effect plays in the structural properties of these alloys. The competition between the fcc and the bcc structures for stability is closely related to the FM exchange in both phases.

Both total energy calculations and present results on paramagnetic neutron scattering indicate that in Fe-Ni alloys \( \Delta E \) between the LS and HS states become smaller as one progresses from anti-Invar to Invar behavior. As \( \Delta E \) becomes smaller the HS state becomes more readily accessed, and therefore lower temperatures are required for substantial FM exchange. On the other hand, the strength of FM exchange in the bcc phase, which is closely related to the variation of the Curie temperature \( T_c \) with composition will also influence the concentration dependence of the bcc-fcc transformation temperature \( T_a \). If \( T_c \) decreases with composition, or barely changes as in the case of Fe-Ni, \( M_a \) decreases due to favorably strong FM exchange in the fcc phase. In Fe-Co \( T_a \) of the bcc phase increases with increasing Co content showing that FM exchange becomes stronger. At the same time, \( \Delta E \) in the fcc phase is expected to decreases slower with increasing Co content than in Fe-Ni, because of the addition of fewer valence electrons per Co atom than in the case of Ni. Therefore, the bcc-fcc transformation of Fe-Co lies at higher temperatures and in a broader temperature range as compared to that of Fe-Ni. One can therefore conclude that the fcc phase of Fe alloys is stabilized with respect to the bcc phase by the FM exchange provided by the HS state.

Acknowledgements

The authors thank H.C. Herper, E. Hoffmann and R. Meyer for many valuable discussions and sublet of theoretical data. Work was supported by the Deutsche Forschungsgemeinschaft through Sonderforschungsbereich SFB 166.

References

15) M. Acet, W. Pepperhoff, and E. F. Wassermann, to be published.
21) E. F. Wassermann: unpublished