

Moment-volume instabilities in $\text{Ti}_x\text{Fe}_{100-x}$ alloys with compositions around the C14 laves phase TiFe_2 *

E.F. Wassermann, B. Rellinghaus, Th. Roessel, J. Kästner^a, and W. Pepperhoff

Tiefemperaturphysik, Universität Duisburg, 47048 Duisburg, Germany

Received: 26 January 1998 / Accepted: 17 April 1998

Abstract. We measured the thermal expansion and the specific heat of $\text{Ti}_x\text{Fe}_{100-x}$ alloys with $x = 30.5$, 32.5 and 35, all with hexagonal C14 laves phase structure (MgZn_2) like TiFe_2 , and determine the temperature dependence of the magnetic contributions to the thermal expansion α_{mag} and the specific heat c_{mag} . For fixed composition $\alpha_{mag}(T)$ and $c_{mag}(T)$ show the same type of behavior, demonstrating that both anomalies are of the same microscopic nature. They originate from moment-volume fluctuations (antiferromagnetic Invar-effect) as a comparison with total energy calculations as a function of atomic volume and moment for TiFe_2 reveals.

PACS. 75.25.+z Spin arrangements in magnetically ordered materials – 75.30.Kz Magnetic phase boundaries – 75.10.Lp Band and itinerant models

1 Introduction

In some recent reviews [1–3] we have demonstrated, how the broad spectrum of structural and magnetic anomalies as well as magnetovolume effects observed in disordered fcc Fe-based 3d-transition metal alloys (*e.g.* Fe-Ni, Fe-Mn or Fe-Pt) can be understood within the framework of *ab-initio* band structure calculations [4–6]. These calculations of magnetic and structural binding surfaces of pure Fe and Fe-based alloys revealed the existence of several, often energetically very close-lying states with different types of magnetic ordering (non-magnetic (NM), ferromagnetic (FM), and antiferromagnetic (AF)) and values of the accompanying moments and volumes (high spin (HS)-, low spin (LS)- or no-moment (NM)-states), in general called moment-volume instabilities. The findings have led to a solution of the almost centennial “Invar problem” [7], the magnetovolume effect typically observed in the thermal expansion of these materials, well-known and of technical importance the FM fcc $\text{Fe}_{65}\text{Ni}_{35}$ alloy. The relation to the structural martensitic transformation observed in most of these alloy systems has also been revealed recently [8].

It is known since a long time that laves phase Intermetallic Compounds (LIC) with Fe-base, like TMFe_2 (TM = Zr, Hf, Ti, Sc), also show more or less strong magnetovolume effects (Invar-like behavior) in their thermal expansion [9], besides a rich spectrum of other magnetic anomalies [10]. It is of general interest to answer the question, if the moment-volume instabilities in these ordered compounds have the same microscopic physical origin as

in the disordered fcc alloys. Of specific interest are alloys of $\text{Ti}_x\text{Fe}_{100-x}$, because under- and overstoichiometric alloys with C14 laves phase structure can be prepared in the range from $\text{Ti}_{29}\text{Fe}_{71}$ to $\text{Ti}_{36.5}\text{Fe}_{63.5}$ [11]. Within this composition range this system shows an abrupt change in the magnetic ordering at $x \sim 32$, with the Fe-rich alloys being predominantly FM and the Ti-rich alloys mainly AF. The relation between structure and magnetism of this system has recently been studied by us in detail [12]. The LIC TiFe_2 is an anisotropic collinear AF, in which only the Fe atoms in the so-called $6h$ positions carry a magnetic moments ($\sim 1.0 \mu_B$) and order ferromagnetically within the $6h$ planes, while the Fe atoms in the so called $2a$ sites (half way between the $6h$ sites) are non-magnetic, close to a moment-volume instability. The Ti atoms in so-called $4f$ positions are also non-magnetic. The overall AF behavior of TiFe_2 results from the AF stacking of the $\text{Fe}6h$ planes. We have shown that the degeneracy of the $\text{Fe}2a$ atoms is lifted, when Ti atoms (with larger atomic volume) are replaced by Fe atoms (with smaller atomic volume). The lattice constants are then reduced and the alloys become FM. *Vice versa*, if Fe atoms are replaced by Ti the lattice constants of the alloys are increased. The alloys, however, remain mainly antiferromagnetically ordered, with some mixed magnetic behavior showing up at low temperatures.

The purpose of the present paper is twofold. Firstly, we want to check whether there is a change in the Invar-like anomalies, when the long range order changes from AF to FM or mixed magnetic behavior in these alloys. We therefore study the thermal expansion behavior of an over ($x = 35$) – and an under-stoichiometric ($x = 30.5$) alloy of this system as well a one with a composition $x = 32.5$, positioned very close to the critical composition for AF

* Dedicated to J. Zittartz on the occasion of his 60th birthday

^a e-mail: kaestner@ttphysik.uni-duisbourg.de

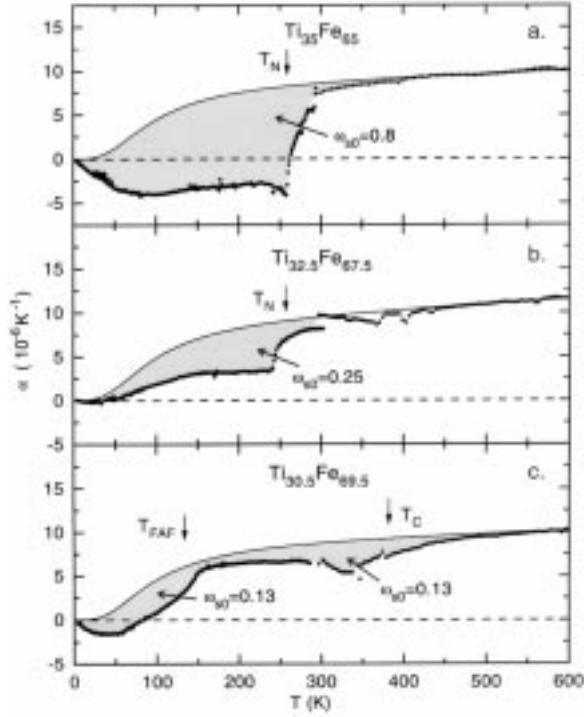


Fig. 1. Thermal expansion coefficient α versus the temperature T as measured on $\text{Ti}_x\text{Fe}_{100-x}$ alloys with hexagonal laves phase C14 structure and $x = 35$ (a), $x = 32.5$ (b), and $x = 30.5$ (c). Full curves: Grüneisen references, fitted to the experimental data at high temperatures above the respective magnetic ordering temperatures (see arrows) using the Debye-temperatures $\theta_D(\infty)$ as determined from the specific heat (see Tab. 1). Shaded areas give the respective spontaneous volume magnetostriction ω_{so} originating from the Invar effect.

to FM behavior. Secondly, we also investigate the specific heat of the three samples, and determine the magnetic contributions to the thermal expansion and the specific heat as a function of the temperature. We compare these results with what has been found for FM Invar systems [13] and check for the nature of the thermal excitations causing the magnetovolume anomalies in both types of Invar systems. Results will be compared with the theoretical predictions for the moment – volume instabilities in TiFe_2 [14].

2 Experimental

The samples have been prepared from high purity Fe (99.98) and Ti (99.7) starting material by arc melting in argon atmosphere. The pellets have been remelted several times for homogeneity. The compositions have been analyzed with atomic absorption spectroscopy on pieces taken from the surface and the inside of each sample. Within the accuracy limit of ± 0.3 at% no deviations from the nominal composition could be detected. Microprobe analysis led to comparable results, so that the nominal concentrations will be used. The samples have been annealed

Table 1. Electronic specific heat at low temperatures, $\gamma(0)$ (from Fig. 3), and at high temperatures, $\gamma(\infty)$ (resulting from the fits in Fig. 2), as well as the respective Debye-temperatures for low temperatures, $\theta_D(0)$ (from Fig. 3) and for high temperatures, $\theta_D(\infty)$ (from Debye-fits to the $c_p(T)$ data in Fig. 2 in the range from 4.2 to ~ 120 K) for three $\text{Ti}_x\text{Fe}_{100-x}$ alloys with hexagonal laves phase C14 structure and $x = 35, 32.5$, and 30.5 .

	$\gamma(0)$ (mJ/mol K ²)	$\gamma(\infty)$ (mJ/mol K ²)	$\theta_D(0)$ (K)	$\theta_D(\infty)$ (K)
$\text{Ti}_{35}\text{Fe}_{65}$	8.5	8.5	423	400
$\text{Ti}_{32.5}\text{Fe}_{67.5}$	9.8	6.3	424	400
$\text{Ti}_{30.5}\text{Fe}_{69.5}$	11.9	5	417	400

in an inductance furnace in Ar atmosphere for 68 hours at 1275 °C in alumina crucibles, sealed in molybdenum tubes. After the heat treatment the samples are cooled to room temperature (RT). X-ray analysis on powdered material showed that all the samples are single phase C14. Traces of possible second phases lie below the sensitivity of the X-ray analysis, *i.e.* below ~ 0.3 at%. For measurements of the thermal expansion cylindrical samples ($l = 7$ mm; $\varnothing = 5$ mm) have been sparc-cut from the ingots. Parallel head faces are achieved by carefully polishing the very brittle samples on a Cu-disc. The thermal expansion is measured in two dilatometers in the range 4.2 to RT and RT to ~ 600 K, respectively, the specific heat in a quasi-adiabatic calorimeter in the range from 4.2 K to 300 K.

3 Results and discussion

3.1 Thermal expansion

Figure 1 shows the thermal expansion coefficient α versus the temperature as determined on the three samples in the range from 4.2 to 600 K. The respective Néel-temperatures and the transition temperature T_{FAF} into a mixed magnetic state for the sample with $x = 30.5$ (all indicated by arrows) have been determined in the magnetic investigations published elsewhere [12]. Grüneisen reference curves (solid lines) are fitted to the $\alpha(T)$ curves at high temperatures $T \gg T_c$, where the magnetovolume effects vanish [13], using the high temperature Debye-temperatures as determined from the specific heat measurements (see Tab. 1). The data in Figure 1 for $\text{Ti}_{35}\text{Fe}_{65}$ show that in the range near T_N a large magnetovolume effect sets in. There is a steep drop in $\alpha(T)$ to negative values, but then down to lower temperatures we find a range, where the thermal expansion is almost constant (temperature independent, “invariable”). This is typical for what is called “antiferromagnetic Invar behavior” (AF-Invar), because it looks very similar to what is found in the classical but FM Invar system $\text{Fe}_{65}\text{Ni}_{35}$ below the respective Curie-temperature [1–3]. The shaded area between the Grüneisen reference and the data points in Figure 1

is equivalent to the volume increase $\Delta V/V$ through the AF-Invar effect at zero temperature relative to the volume of the NM Grüneisen reference. This property is called the “spontaneous volume magnetstriction” ω_{so} in the literature [1–3]. The absolute value of ω_{so} is 0.8 for the AF $\text{Ti}_{35}\text{Fe}_{65}$ Invar in Figure 1 is about half as compared to FM-Invar $\text{Fe}_{65}\text{Ni}_{35}$.

Figure 1 shows that the AF-Invar effect is reduced to $\omega_{so} = 0.25$ in the alloy $\text{Ti}_{32.5}\text{Fe}_{67.5}$ ($T_N = 255$ K). Reason is the increase of the Fe concentration, which leads to a reduction of the strength of the AF ordering through the presence of FM components, as our recent investigation have shown [12]. Further increase of the Fe concentration leads to the formation of more FM clusters in the C14 $\text{Ti}_x\text{Fe}_{100-x}$ alloys. At the composition $\text{Ti}_{30.5}\text{Fe}_{69.5}$ these clusters form a contiguous network, so that there is now a FM long range order present below the Curie-temperature $T_c = 380$ K [12]. We can see from Figure 1 that a magnetovolume effect goes along with this FM ordering *i.e.* the sample shows the FM-Invar effect with $\omega_{so} = 0.13$ in the range below T_c . If the temperature is decreased further, there is a mixed magnetic ordering observed in $\text{Ti}_{30.5}\text{Fe}_{69.5}$ below a temperature we call T_{FAF} . Figure 1 reveals that a magnetovolume effect also occurs in that region ($\omega_{so} = 0.13$).

The data in Figure 1 can basically be understood within the results of the calculations of the AF and FM binding surfaces (total energy as a function of the volume and the magnetic moment) for the Fe6*h* atoms of C14 TiFe_2 [14]. According to these calculations the ground state of TiFe_2 is the AF state, and remains to be energetically the lowest state, if the volume is increased. This is indeed found experimentally, because we observe that on increase of the lattice constant (increase of the Ti concentration) the alloys in $\text{Ti}_x\text{Fe}_{100-x}$ are always AF ordered. Theoretically [14], there is an FM state lying energetically very close to the AF state (0.1 mRy/atom). This FM state becomes the ground state in TiFe_2 on reduction of the atomic volume [14]. This is also in accordance with our experimental findings [12], showing that on decrease of the Ti concentration and simultaneously a decrease of the lattice constant below $x = 32$ the alloys are FM. In both binding surfaces of TiFe_2 in reference [14] there are moment-volume instabilities with Invar-typical anharmonicities at lower volumes than the equilibrium volume (low spin (LS) to no-moment (NM)) transitions) in the FM and the AF state for the Fe6*h* atoms. But there are also anharmonicities at higher volumes, equivalent to LS- to high spin (HS)-transitions especially in the FM binding surface. This would call for “Anti-Invar” behavior [15], something not observed in the alloys in Figure 1. However, one should not forget that in the over- and both under-stoichiometric compositions in Figure 1 also the Fe2*a* atoms become polarized and in total the spin structure of the alloys is not colinear, so that the results in reference [14] cannot explain in detail the Invar properties as measured experimentally.

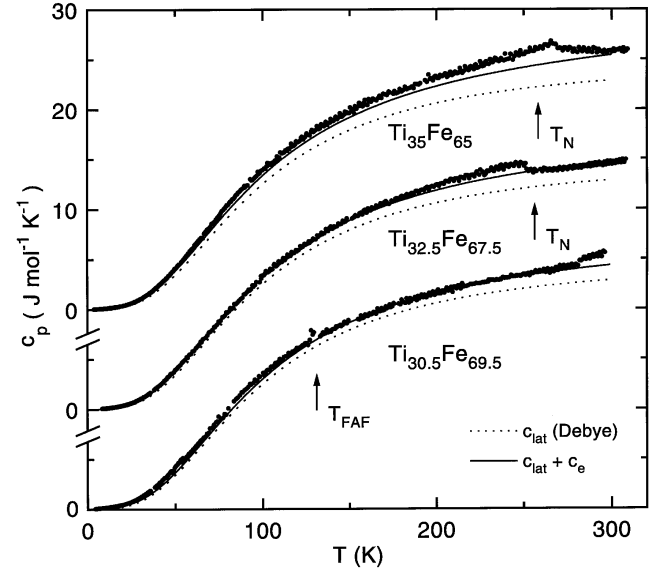


Fig. 2. Total specific heat c_p versus temperature T as measured on the same TiFe alloys as in Figure 1 (curves for $x = 32.5$ and $x = 35$ are shifted upwards by 10 J/mol K). Dotted curves indicate the Debye-like behavior of the lattice c_{lat} , full curves give the sum of the lattice and the electronic contribution $c_{lat} + c_{el}$, fitted to the experimental curves at high temperatures (for resulting high temperature electronic $\gamma(\infty)$ -values see Tab. 1).

3.2 Specific heat

Figure 2 shows the total specific heat c_p as measured as a function of temperature on the same three TiFe C14 samples as in Figure 1. Note the absence of sharp anomalies (which would be typical for a phase transition of second order) at the respective Néel-temperatures. This is an Invar-typical feature as we have discussed in detail earlier [13]. In the sample with $x = 30.5$ the Curie-temperature $T_c = 380$ K lies above the range which can be reached in our calorimeter. Moreover, an anomaly at the transition temperature $T_{FAF} = 130$ K into the mixed magnetic state (*cf.* Fig. 1) can not be observed in the specific heat of this sample. Figure 3 gives the low temperature data in the usual plot of c_p/T versus T^2 , so that the respective low temperature γ^0 -values and Debye-temperatures θ_D^0 can be determined. Data are summarized in Table 1. After subtraction of the electronic contribution, fits of Debye curves to the low temperature experimental data in Figure 2 result in small temperature dependences of the Debye-temperatures (results not shown here). Values drop from θ_D^0 in the range 4.2–20 K to θ_D^∞ in the range around 120 K. Values are also given in Table 1. These θ_D^∞ values have been used in Figure 1 for the Grüneisen fits.

To determine the magnetic contribution c_{mag} to the specific heat we assume that all contributions to the specific heat are additive, *i.e.* $c_p = c_{el} + c_{lat} + c_{mag}$. That this is a reasonable assumption has been discussed earlier [13]. Since the bulk modulus of our TiFe C14 alloys is not known we cannot account for the contribution $c_p - c_v$.

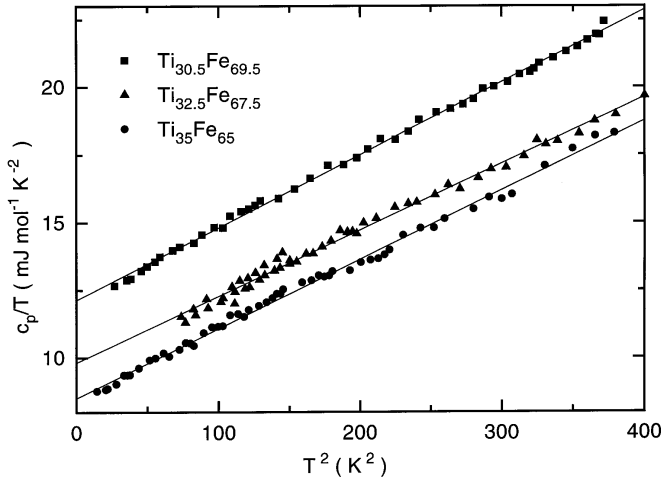


Fig. 3. Total specific heat divided by the temperature c_p/T versus T^2 for the three TiFe alloys as in Figure 2. The resulting low temperature electronic terms, $\gamma(0)$, of the specific heat and the low temperature Debye-temperatures $\theta(0)$ are given in Table 1.

Dotted curves in Figure 2 give the Debye lattice contributions. The full curves in Figure 2 are the sum of ($c_{lat} + c_{el}$), fitted to the experimental data at high temperatures, *i.e.* in the range where the magnetovolume effects vanish. From these fits some high temperature γ^∞ -values for our TiFe alloys result, which are also given in Table 1. These γ^∞ -values are smaller than the low temperature γ^0 -values, a fact which has also been observed and discussed in detail for other Invar systems earlier [13]. Reason is the enhanced electron-phonon interaction at low temperatures [13] and possibly low energy magnetic excitations, especially in the alloy $\text{Ti}_{30.5}\text{Fe}_{69.5}$ with mixed magnetic order below T_{FAF} . We also mention that Wang *et al.* [16] found $\gamma^\infty = 6.5$ mJ/mol K^2 for a stoichiometric TiFe_2 sample from high temperature (up to 700 K) specific heat measurements, supporting our findings that $\gamma^\infty < \gamma^0$.

In Figure 4 we plot the magnetic contributions to the specific heat $c_{mag} = c_p - c_{el} - c_{lat}$ (top panels) as well as in the thermal expansion α_{mag} (bottom panels; differences between the Grüneisen references and the data points taken positively; see shaded areas in Fig. 1) versus the temperature. The panels on the left side give the respective results for the sample with $x = 35$, the panels in the middle those for the sample with $x = 32.5$, and the panels on the right side those for $x = 30.5$. A comparison between the respective anomalies in all three samples in Figure 4 immediately reveals that the magnetic anomalies in the specific heat $c_{mag}(T)$ and in the thermal expansion $\alpha_{mag}(T)$ are very similar in their overall behavior. Both types of anomalies occur simultaneously, within the same temperature range, and at the same maximum temperatures in $c_{mag}(T)$ and $\alpha_{mag}(T)$. The latter are slightly smaller than the values as determined in the magnetic investigations [12]. The results in Figure 4 give strong evidence for the assumption that the anomalies $c_{mag}(T)$ and $\alpha_{mag}(T)$ are caused by the same

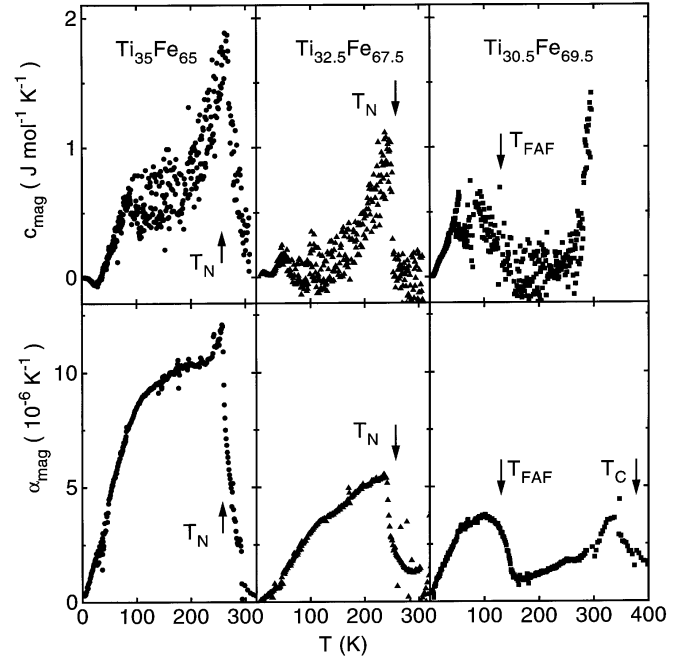


Fig. 4. Top panels: magnetic contributions $c_{mag}(T)$ to the specific heat as determined from the data in Figure 2 ($c_{mag} = c_p - c_{lat} - c_{el}$); bottom panels: magnetic contributions to the thermal expansion α_{mag} as determined from the data in Figure 1 (shaded areas, positively plotted) for the three TiFe samples with $x = 35$ at% Ti (left side panels), $x = 32.5$ (middle panels), and $x = 30.5$ (right side panels). The anomalies originate from moment-volume fluctuations in all three samples. Note the similarities in the temperature behavior for fixed composition in both types of anomalies, $c_{mag}(T)$ and $\alpha_{mag}(T)$, and also the analogies in the behavior, if the different compositions are compared. For further details see text.

type of thermal excitations, with the same physical nature. Since analogous similarities in $c_{mag}(T)$ and $\alpha_{mag}(T)$ have been found by us for FM FePt Invar alloys [13], we can even state that these excitations are of the same nature in FM- and AF-Invar, *i.e.* they are independent of the type of existing magnetic long range order. We call these excitations “moment-volume fluctuations”, characterized by transitions between the high-spin ground state, with large volume and large moment, to the low spin state with smaller atomic volume and smaller moment at higher temperatures. The energetic difference between these states is of the order of 1 mRy \sim 150 K [3–6,14]. The basic physical nature are charge fluctuations between anti-bonding t_{2g} – and non-bonding e_g – electronic levels at the Fermi energy [1–3]. The results in Figure 4 show that the excitations start at zero temperature and also reach into the range above the ordering temperatures, where the alloys are paramagnetic. This has also been found on FM FePt [13] and FeNi [17] Invar. The existence of ferromagnetic spin fluctuations in the paramagnetic range of FeNi alloys has been recently shown by us experimentally [18]. Yet, first principles finite temperature calculations

are certainly necessary to explain the temperature dependence of the moment-volume fluctuations in detail.

4 Summary

We have demonstrated that by changing the magnetic long range order from predominantly AF at $x = 35$ to predominantly FM at $x = 30.5$ in $\text{Ti}_x\text{Fe}_{100-x}$ alloys with laves phase C14 structure the magnetovolume effect changes from AF-Invar to FM-Invar in the thermal expansion. This is to our knowledge the only system showing such a rapid change in the Invar behavior by a small variation of the Fe concentration of only 4.5 at%. The results are *grosso modo* in accordance with theoretical calculations of the binding surfaces for AF and FM TiFe_2 with C14 structure, showing Invar typical anharmonicities in the total energy curves projected into the moment-volume plane [14]. Comparison of the magnetic contributions to the thermal expansion and the specific heat on the present TiFe alloys reveals that the temperature dependence of both types of anomalies is very similar. This proves that the moment-volume fluctuations, which are the origin of the observed anomalies, have the same influence on both properties. Similar investigation on the classical FM Invar systems FeNi [17] and FePt [13] have lead to an analogous result. One can therefore conclude that the origin of the Invar effect in $\text{Ti}_x\text{Fe}_{100-x}$ alloys with laves phase C14 structure is the same as in disordered fcc FeNi or all the other fcc Fe-based alloys showing the Invar effect [1–6]. Microscopic origin are charge fluctuations between electronic levels with different symmetry (t_{2g} and e_g) and anti-bonding or non-bonding character. What type of instability effect (Invar [1–6], so-called “Anti-Invar” [15] or martensite [8]) occurs in whatever system at a given composition is only a question of the position of the Fermi-energy relative to these levels, *i.e.* a question of the electron concentration per atom. How an effect manifests itself as a function of temperature is a question of the different strength of the t_{2g} - and e_g - electron-phonon coupling. First principles finite temperature calculations are necessary to explain the details. The anomalous behavior is certainly not bound to the thermal expansion and specific heat but should also be found in *e.g.* the elastic constants, the bulk modulus and forced volume magnetostriction [1–3]. These properties can, however, not be measured on TiFe alloys with C14 structure, since respective single crystals can not be prepared.

The authors thank P. Stauche, M. Brinkmann and H. Bach for preparation of the samples. Helpful discussions with P. Entel and his group are also gratefully acknowledged. Work was supported by the Deutsche Forschungsgemeinschaft within SFB 166.

References

1. E.F. Wassermann, in *Ferromagnetic Materials*, Vol. V, edited by K.H.J. Buschow, E.P. Wohlfarth (North-Holland, Amsterdam, 1990) p. 240.
2. E.F. Wassermann, *J. Magn. Magn. Mater.* **100**, 346 (1991).
3. E.F. Wassermann, P. Entel, *J. Phys. IV Colloq. France* **5**, C8-287 (1995).
4. P. Entel, E. Hoffmann, P. Mohn, K. Schwarz, V.L. Moruzzi, *Phys. Rev. B* **47**, 8706 (1993).
5. M. Schröter, H. Ebert, H. Akai, P. Entel, E. Hoffmann, G.G. Reddy, *Phys. Rev. B* **52**, 188 (1995).
6. P. Entel, H.C. Herper, K. Kadau, R. Meyer, E. Hoffmann, G. Nepecks, M. Acet, W. Pepperhoff, in *Novel Materials*, edited by B.K. Rao (Nova Science, New York, 1998).
7. E.F. Wassermann, in *The Invar Effect: A Centennial Symposium*, edited by J. Wittenauer (The Minerals, Metals and Mining Society, Warrendale (PA) USA, 1997), p. 51.
8. P. Entel, E. Hoffmann, M. Clossen, K. Kadau, M. Schröter, R. Meyer, H.C. Herper, M.S. Yang, in *The Invar Effect: A Centennial Symposium*, edited by J. Wittenauer (The Minerals, Metals and Mining Society, Warrendale (PA) USA, 1997), p. 87.
9. Y. Muraoka, M. Shiga, Y. Nakamura, *J. Phys. Soc. Jpn Lett.* **40**, 905 (1976).
10. Y. Nishihara, *J. Mag. Magn. Mat.* **70**, 75 (1987).
11. W. Brückner, K. Kleinstück, G.E.R. Schulze, *Phys. Stat. Sol.* **23**, 475 (1967).
12. E.F. Wassermann, B. Rellinghaus, M. Acet, W. Pepperhoff, J.M.M.M. (to be published).
13. B. Rellinghaus, J. Kästner, T. Schneider, E.F. Wassermann, P. Mohn, *Phys. Rev. B* **51**, 2983 (1995).
14. E. Hoffmann, P. Entel, E.F. Wassermann, K. Schwarz, P. Mohn, *J. Phys. IV Colloq. France* **5**, C2-117 (1995).
15. T. Schneider, M. Acet, B. Rellinghaus, E.F. Wassermann, W. Pepperhoff, *Phys. Rev. B* **51**, 8917 (1995II).
16. H. Wang, R. Lück, B. Predel, *Z. Metallkd.* **84**, 230 (1993).
17. J. van Lier, J. Kästner, E.F. Wassermann, (to be published).
18. M. Acet, E.F. Wassermann, K. Andersen, A. Murani, O. Schärpff, *Euro. Phys. Lett.* **40**, 93 (1997).