chapter 3

INVAR:
MOMENT–VOLUME INSTABILITIES
IN TRANSITION METALS AND
ALLOYS

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1. Introduction and outline of the Invar problem

The 'Invar effect' originates from investigations by Ch.E. Guillaume who found, already in 1897, that ferromagnetic fcc FeNi alloys at concentrations around Fe_{65}Ni_{35} show almost constant – 'invariant' – thermal expansion as a function of temperature in a wide range around room temperature (Guillaume 1897). According to his results the linear thermal expansion coefficient \( \alpha = (1/l)/(dl/dT) \) of Fe_{65}Ni_{35} Invar at 300 K is about \( 1.2 \times 10^{-6} \) K\(^{-1} \), thus an order of magnitude smaller than in the pure components Fe and Ni and even smaller than in a Pt–10% Ir alloy, the material used for the prototype meter defined since 1875. The practical importance of Guillaume's detection for the construction of precision instruments and seismographic devices as well as his finding of the temperature-independent elastic behavior of \( \gamma \)-FeNiCr alloys (Guillaume 1920) – named 'Elinvar' and used (with some precipitation-hardening additions) as hair spring material in watches – honoured him with the Nobel prize in 1920.

Figure 1a schematically shows the relative volume (or length) change \( \omega = \Delta V/V \) with temperature for an Fe_{65}Ni_{35} Invar alloy. The full curve gives \( \omega_{\text{exp}}(T) \) as determined experimentally. It can be seen that, with respect to a nonmagnetic ('hypothetic') reference sample (\( \omega_{\text{nm}}(T) \), dashed curve), the Fe_{65}Ni_{35} Invar alloy has a positive magnetovolume effect below the Curie temperature \( T_C \). The difference \( \omega_{\text{exp}}(T) - \omega_{\text{nm}}(T) = \omega_s(T) \) is called the spontaneous volume magnetostriction (dashed-dotted curve in fig. 1a), with a maximum value at \( T=0 \) of \( \omega_{s0} = 1.9 \times 10^{-2} \) for Fe_{65}Ni_{35}. Values of the same order of magnitude are found in other Invar systems, as we shall see later.

Figure 1b shows the temperature dependence of the thermal expansion coefficient \( \alpha(T) \) as derived from fig. 1a. The full curve gives \( \alpha_{\text{exp}}(T) \) as determined from \( \omega_{\text{exp}}(T) \). The dashed curve shows the temperature dependence of the nonmagnetic reference sample, \( \alpha_{\text{nm}}(T) \), as calculated from the Grüneisen relation, using data from specific-heat measurements. (The problem of finding a reference sample from first principles will be discussed later.) Assuming that \( \alpha_{\text{exp}}(T) = \alpha_{\text{nm}}(T) + \alpha_m(T) \), where \( \alpha_m(T) \) denotes the magnetic contribution to the thermal expansion (dashed-dotted line in fig. 1b), one can see that in this type of analysis, \( \alpha_m(T) \) is negative throughout the range from zero Kelvin to above the Curie temperature \( T_C \).

Ch.E. Guillaume (1897) also determined the concentration dependence of \( \alpha_{\text{exp}} \)
at constant temperature in the FeNi system. Figure 2 shows that, at room temperature and a concentration of 35 at% Ni, $\alpha_{\text{exp}}$ reaches its smallest value (‘Invar effect’). Anomalies in $\alpha$, although increasingly smaller, are, however, also present in alloys containing up to 75 at% Ni. For concentrations below about 33 at% Ni, a structural transition from the fcc $\gamma$-phase to the bcc $\alpha$-phase (which does not show the Invar effect) occurs, so that the data are no longer reliable. Figure 2 also reveals that close to the $\gamma-\alpha$ transition, where $\alpha$ is minimum, the
spontaneous volume magnetostriction $\omega_{q0}$ reaches maximum values. However, nearness to a $\gamma-\alpha$ transition is not a necessary condition for the occurrence of the Invar effect, as we shall see below.

Returning to fig. 1b and the temperature dependence of the expansion coefficient, two remarks should be added. First, at low temperatures $\alpha_{exp}(T)$ is negative and has a minimum. This means that the sample first shrinks when raising the temperature from $T = 0$. This minimum in $\alpha_{exp}(T)$ is not Invar typical as we have demonstrated recently (Wassermann 1989b). Second, concerning the high-temperature behavior, one can see that around and above the Curie temperature $T_C$ (arrow in fig. 1), the expansion anomaly does not vanish (nor has any sharp 'features'). This has to be explained in any type of model describing the Invar effect.

A further example for the extraordinary properties of Invar at higher temperatures is given in fig. 3, where the heat capacity $C_p(T)$ for three FeNi alloys as measured by Bendick et al. (1978) in the temperature range 300–1200 K is shown. Above the 'Grüneisen' background (broken line), which refers in the same way as

![Fig. 3. Specific heat $C_p$ as a function of temperature as measured by Bendick et al. (1978) on three FeNi alloys. The respective Curie temperatures are marked by arrows. The temperature dependence of $C_p$ for respective non-magnetic reference samples are shown by the dashed horizontal lines. The dashed-dotted lines give $C_p(T)$ as calculated for FeNi by Kakehashi (1981) within the finite-temperature local-environment model (see section 6.2).](image-url)
### TABLE 1
Invar- and Elinvar systems.

<table>
<thead>
<tr>
<th>fcc structure</th>
<th>$\gamma$-range at 20°C</th>
<th>Magnetic Order</th>
<th>Magnetic phase diagram</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{1-x}$Ni$_x$</td>
<td>$0.3 \leq x \leq 1.0$</td>
<td>FM (SG)</td>
<td>Fig. 5</td>
</tr>
<tr>
<td>Fe$_{1-x}$Pt$_x$ diso.</td>
<td>$0.25 \leq x \leq 0.5$</td>
<td>FM</td>
<td>Fig. 6</td>
</tr>
<tr>
<td>Fe$_{1-x}$Pt$_x$ ord.</td>
<td>$0.23 \leq x \leq 0.5$</td>
<td>FM</td>
<td>Fig. 6</td>
</tr>
<tr>
<td>Fe$_{1-x}$Pd$_x$ diso.</td>
<td>$0.3 \leq x \leq 0.6$</td>
<td>FM</td>
<td>Fig. 7</td>
</tr>
<tr>
<td>Fe$_{1-x}$Mn$_x$</td>
<td>$0.2 \leq x \leq 0.58$</td>
<td>AF</td>
<td>Fig. 8</td>
</tr>
<tr>
<td>Ni$_{1-x}$Mn$_x$ diso.</td>
<td>$0 \leq x \leq 0.45$</td>
<td>FM-SG</td>
<td>Fig. 9</td>
</tr>
<tr>
<td></td>
<td>$0.6 \leq x \leq 0.8$</td>
<td>AF</td>
<td>Fig. 9</td>
</tr>
<tr>
<td>Co$_{1-x}$Mn$_x$</td>
<td>$0.27 \leq x \leq 0.5$</td>
<td>FM-SG-AF</td>
<td>Fig. 10</td>
</tr>
<tr>
<td>Co$_{1-x}$Fe$_x$</td>
<td>$0.05 \leq x \leq 0.25$</td>
<td>FM</td>
<td>Fig. 11</td>
</tr>
<tr>
<td>Co$_{1-x}$Ni$_x$</td>
<td>$0.2 \leq x \leq 1$</td>
<td>FM</td>
<td>Fig. 11</td>
</tr>
<tr>
<td>(Fe$<em>{1-x}$Ni$<em>y$)$</em>{Cr</em>{1-y}}$</td>
<td>See resp. fig.</td>
<td>FM-SG-(AF)</td>
<td>Fig. 13</td>
</tr>
<tr>
<td>(Fe$<em>{1-x}$Ni$<em>y$)$</em>{Mn</em>{1-y}}$</td>
<td>See resp. fig.</td>
<td>FM-SG-AF</td>
<td>Fig. 14</td>
</tr>
<tr>
<td>(Fe$<em>{1-x}$Ni$<em>y$)$</em>{Co</em>{1-y}}$</td>
<td>See resp. fig.</td>
<td>FM</td>
<td>Fig. 15</td>
</tr>
<tr>
<td>(Co$<em>{1-x}$Mn$<em>y$)$</em>{Fe</em>{1-y}}$</td>
<td>See resp. fig.</td>
<td>FM-SG-AF</td>
<td>Fig. 16</td>
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<tr>
<td>(Co$<em>{1-x}$Mn$<em>y$)$</em>{Ni</em>{1-y}}$</td>
<td>See resp. fig.</td>
<td>FM-SG-AF</td>
<td>Fig. 17</td>
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<tr>
<td>(Co$<em>{1-x}$Fe$<em>y$)$</em>{Cr</em>{1-y}}$</td>
<td>See resp. fig.</td>
<td>FM</td>
<td>Fig. 18</td>
</tr>
<tr>
<td>(Fe$_{1-x}$Ni$<em>y$)$</em>{Fe(Cu, V)_8}$</td>
<td>$0.29 \leq x \leq 0.4$</td>
<td>FM</td>
<td>-</td>
</tr>
<tr>
<td>Fe$<em>{70}$(Pt$</em>{1-x}$Re$<em>x$)$</em>{30}$</td>
<td>$0.1 \leq x \leq 0.17$</td>
<td>FM</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>bcc structure</th>
<th>$\alpha$-range at 20°C</th>
<th>Magnetic order</th>
<th>Magnetic phase diagram</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$_{1-x}$Fe$_x$</td>
<td>$0 \leq x \leq 1.0$</td>
<td>FM-SG-AF</td>
<td>Fig. 12</td>
</tr>
<tr>
<td>Cr$_{1-x}$Mn$_x$</td>
<td>$0 \leq x \leq 0.6$</td>
<td>AF</td>
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<table>
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<th>hex. structure</th>
<th>$\varepsilon$-range at 20°C</th>
<th>Magnetic order</th>
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</thead>
<tbody>
<tr>
<td>Co$_{1-x}$Cr$_x$</td>
<td>$0 \leq x \leq 0.15$</td>
<td>FM</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>amorphous structure</th>
<th>Components</th>
<th>Magnetic order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{1-x}$ET$_x$</td>
<td>ET: Sc, Y, Zr, Hf, La</td>
<td>FM, SG</td>
</tr>
<tr>
<td>Fe$_{1-x}$B</td>
<td></td>
<td>FM</td>
</tr>
<tr>
<td>Fe$_{1-x}$P</td>
<td></td>
<td>FM</td>
</tr>
<tr>
<td>(Fe$<em>{1-x}$TM$<em>x$)$</em>{75-80}$G$</em>{25-20}$</td>
<td>TM: Cr, Mn, Co, Ni</td>
<td>FM-SG</td>
</tr>
<tr>
<td>G: Si, B, P</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Laves phases and Intermetallic compounds

<table>
<thead>
<tr>
<th>Components</th>
<th>Magnetic order</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETFe$_2$</td>
<td>ET: Sc, Ti, Zr, Hf</td>
</tr>
<tr>
<td>RECO$_2$</td>
<td>RE: Gd, Tb; Dy, Ho, Er</td>
</tr>
<tr>
<td>(Zr$_{1-x}$Nb$_x$)Fe$_2$</td>
<td></td>
</tr>
<tr>
<td>Zr(Fe$_{1-x}$Co$_x$)$_2$</td>
<td></td>
</tr>
<tr>
<td>RE$<em>2$Fe$</em>{14}$B</td>
<td>RE: all except Eu</td>
</tr>
<tr>
<td>RE$_2$Fe$_7$</td>
<td>RE: Y, Dy, Lu</td>
</tr>
<tr>
<td>Dy$<em>2$(Fe$</em>{1-x}$Co$<em>{1-x}$)$</em>{17}$</td>
<td></td>
</tr>
<tr>
<td>Dy$<em>2$(Fe$</em>{1-x}$Al$<em>{1-x}$)$</em>{17}$</td>
<td></td>
</tr>
<tr>
<td>LaFe$_{13-15}$Al$_x$</td>
<td></td>
</tr>
</tbody>
</table>
in figs. 1a,b to a nonmagnetic reference alloy, there is in addition to the magnetic specific heat, which peaks at the respective $T_c$ values, a considerable excess specific heat-capacity due to the Invar effect. Characteristically, a broad ‘bump’ in $C_p(T)$ occurs around 500 K in all three alloys. Similar effects have been encountered by the same authors in other Invar alloys like, e.g., Fe$_{50}$Ni$_{1-x}$Mn$_{x}$ (as will be seen fig. 41) or Fe$_{80-x}$Ni$_x$Cr$_{20}$ (Bendick and Pepperhoff 1981). Note that for Fe$_{65}$Ni$_{35}$, where $T_c$ coincides with the ‘bump’, the $\lambda$-type anomaly in $C_p(T)$ is washed out.

The original work by Guillaume was the basis for widespread experimental and theoretical activities, in the 1950s and 1960s especially in Japan and Europe, and with the increasing understanding of solid-state magnetism, the number of publications about Invar and Invar-related topics increased drastically. The reason for this increase was two-fold. First, the observation of Invar anomalies remained by no means bound to ferromagnetic fcc FeNi alloys. As shown in table 1, Invar anomalies are, to date, observed in ferromagnetic (FM) as well as antiferromagnetic (AF) binary, ternary (and also multi-component) alloy systems. The lattice structure is of no influence, and Invar systems can have fcc, bcc, hexagonal and other structures (e.g., fct) or even be amorphous. Moreover, Invar anomalies are observed in rare earth (RE)-transition metal (TM) compounds with Lavesphase structure, e.g., RECo$_2$ or compounds like Fe$_{14}$Nd$_2$B. The key point is that the systems are rich in at least one (but a specific, as we shall see later) 3d-transition element. There are no purely 4f (nor insulating) Invar alloys or compounds. This shows that the Invar effect is obviously a problem of itinerant 3d-magnetism.

Secondly, although the name Invar resulted from the anomaly in the thermal expansion, a broad variety of physical anomalies have, to date, to be considered as Invar typical. Table 2 lists the main physical properties in which Invar anomalies are observed, as a function of composition and variable external

<table>
<thead>
<tr>
<th>Property</th>
<th>Variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal expansion</td>
<td>$(\Delta l/l)(T)$, $\alpha(T)$</td>
</tr>
<tr>
<td>Lattice constant</td>
<td>$a(T)$</td>
</tr>
<tr>
<td>Spontaneous volume magnetostriction</td>
<td>$\omega_s = (\Delta V/V)(T)$</td>
</tr>
<tr>
<td>Spontaneous volume magnetostriction at $T = 0$</td>
<td>$\omega_s(T = 0) = \omega_o$</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>$c_v(T)$</td>
</tr>
<tr>
<td>Derivative of the electrical resistivity</td>
<td>$d\rho/dT$</td>
</tr>
<tr>
<td>Magnetization</td>
<td>$(M/M_0)(T)$</td>
</tr>
<tr>
<td>Hyperfinefield distribution</td>
<td>$P(B_{HF})$</td>
</tr>
<tr>
<td>Forced volume magnetostriction</td>
<td>$(\delta \omega/\delta H)(T)$</td>
</tr>
<tr>
<td>High-field susceptibility</td>
<td>$x_{HF}(T)$</td>
</tr>
<tr>
<td>Pressure dependence of magnetization</td>
<td>$-(dM/dp)_{T,\text{H}}$</td>
</tr>
<tr>
<td>Pressure dependence of Curie temperature</td>
<td>$-(dT_c/dp)$</td>
</tr>
<tr>
<td>Pressure dependence of Néel temperature</td>
<td>$-(dT_N/dp)$</td>
</tr>
<tr>
<td>Young and bulk modulus</td>
<td>$E(T)$, $B(T)$</td>
</tr>
<tr>
<td>Elastic constants</td>
<td>$C_1(T), C_{44}(T), C'(T)$</td>
</tr>
<tr>
<td>Neutron scattering</td>
<td>$D(T), \omega(k, T)$</td>
</tr>
</tbody>
</table>
parameters like temperature, magnetic field and pressure. The listings in tables 1 and 2 demonstrate the richness of the Invar effect and, at the same time, the complexity incorporated. Earlier reviews summarizing the field have been given in the literature (Nakamura 1976, Honda Memorial Series on Material Science, No. 3, 1978, Freeman and Shimizu 1979, Shimizu 1979, 1983). Recent updatings on the physical understanding of Invar have been given by Wassermann (1987, 1989 a,b) and in the proceedings of the International Symposium on Magneto-elasticity and Electronic Structure of Transition Metals, Alloys and Films (ISOMES), which took place in Spring 1989 in Duisburg, FRG (Wasserman et al. 1989).

Finally, we mention here that the name ‘Invar’ is somewhat misleading in describing all the observed anomalies. ‘Invar’ stands for alloys showing minimum thermal expansion coefficients (maximum spontaneous volume magnetostriction) in certain ranges of composition and temperatures (cf. Fe\textsubscript{65}Ni\textsubscript{35} in fig. 2). A more general headline, summarizing all the features in a better way would be: ‘moment–volume instabilities in 3d-element rich systems’. The relevance of this will be shown in section 6.

2. Technical applications of Invar- and Elinvar-type alloys

Since their discovery, Invar- and Elinvar-type alloys have experienced increasing technical applications. Although the annual production of these materials has never been very high (as compared, e.g., to stainless steel) and the total amount produced world wide to date is difficult to figure (we estimate $10^4$–$10^5$ tons per year), one can see from table 3 that the practical use of Invar and Elinvar is widespread.

As shown in table 3, two major fields for technical applications can be distinguished. First, there is a group of materials, which meets the requirement of dimensional stability with temperature, i.e., low thermal expansion coefficients. To this group belong the classical FeNi Invar alloys (Guillaume 1897), the so-called ‘Super-Invar’ alloys, which are ternary FeNiCo alloys with 35 at% Ni and 4–6 at% Co (Masumoto 1931), and ‘Stainless-Invar’ (Masumoto 1934), which are ternary Co-rich alloys of CoFeCr with roughly 9 at% Cr and 52 at% Co.

| Requirement: dimensional stability |
| Bi-metals; wires for printers and x–y recorders; liquid natural gas (LNG) tanks and pipelines; precision machine tools; precision pendulums; precision capacitors; precision moulds; transistor bases; lead frames for integrated circuits; membranes; springs; glass (ceramic)–metal seals; pressure gauges; thermostats; bending meters; gravity meters; flow meters; astronomical telescopes; seismographic devices; microwave guides; resonant cavities; laser light sources; radar echo boxes. |

| Requirement: elastic stability |
| springs; segments, plates and wires for watches, chronometers, time recording instruments and various electronic and electromagnetic instruments; vibrators for standard frequencies; mechanical filters; reeds; reed relays; tuning forks; filters; delay lines. |
The second class of materials is used for practical purposes, where stability of the elastic behavior (bulk- and shear modulus) with temperature is required. These materials often show low thermal expansivity too. To this group belong the classical Elinvar alloys of FeNi (40–45 at% Ni), ternary alloys of FeNiCr (5–12 at% Cr) detected by Guillaume (1920), and the so-called ‘Super-Elinvar’ (39 at% Ni, 10 at% Co, 10 at% Cr, Fe balance).

In 1952, Masumoto and Saito (1952) found that annealed ternary alloys with compositions in the neighborhood of Stainless-Invar (cf. table 4) show high elasticity but small temperature coefficients of the Young- and shear moduli. These alloys were named ‘Co-Elinvar’, since they are Elinvar-type alloys containing cobalt. With the addition of Ni, the concentration range of low shear- and Young-modulus coefficients can be widened, so that there are also Co-Elinvar-type alloys in the quarternary system FeNiCoCr (Masumoto et al. 1954). In table 4 we have summarized the concentration ranges of the 3d-element constituents of the major Invar and Elinvar type alloys used technically and mentioned before. All these alloys have fcc \( \gamma \)-type structure and they are ferromagnetic. Figure 4 shows, albeit in a qualitative way, where these alloys are positioned in the quarternary constitution diagram of FeNiCoCr. The diagram demonstrates the linear law of substitution of Co and Cr by Ni in both series, from Stainless-Invar to Super-Invar and Co-Elinvar to Super-Elinvar for the minimum temperature coefficients of thermal expansion and shear modulus, respectively (Masumoto et al. 1956).

If the alloys listed in table 4 would consist of the 3d-elements only, they would not meet the necessary requirements for technical application, mainly because

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition (Fe balance)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Invar</td>
<td>Ni(at%) Co(at%) Cr(at%) Mn(at%)</td>
<td>Additions for hardening and prevention of aging (in concentrations ( \leq 0.5 ) at%): Be, Mn, Mo, Si, Se</td>
</tr>
<tr>
<td>Super-Invar</td>
<td>31–33 4–6 – –</td>
<td>Cr replaceable by Mo, W.</td>
</tr>
<tr>
<td>Stainless-Invar</td>
<td>– 52–54 9–10 –</td>
<td>Additions for hardening and reduction of ( \Delta E )-effect: Ti, Be, Al</td>
</tr>
<tr>
<td>Elinvar</td>
<td>40–44 – – –</td>
<td></td>
</tr>
<tr>
<td>Super-Elinvar</td>
<td>36–38 5–10 5–10 –</td>
<td></td>
</tr>
<tr>
<td>Co-Elinvar</td>
<td>36–39 5–10 9–10 –</td>
<td>Velinvar (V for Cr)</td>
</tr>
<tr>
<td></td>
<td>9–25 20–35 10–12 –</td>
<td>Moelinvar (Mo for Cr)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thungelinvar (W for Cr) and/or additions for Ti, Mn, Si, Al</td>
</tr>
</tbody>
</table>

**TABLE 4**

Commercial Invar- and Elinvar-type alloys.

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition (Fe balance)</th>
<th>Remarks</th>
</tr>
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<tbody>
<tr>
<td>Invar</td>
<td>Ni(at%) Co(at%) Cr(at%) Mn(at%)</td>
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<td>31–33 4–6 – –</td>
<td>Cr replaceable by Mo, W.</td>
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<tr>
<td>Stainless-Invar</td>
<td>– 52–54 9–10 –</td>
<td>Additions for hardening and reduction of ( \Delta E )-effect: Ti, Be, Al</td>
</tr>
<tr>
<td>Elinvar</td>
<td>40–44 – – –</td>
<td></td>
</tr>
<tr>
<td>Super-Elinvar</td>
<td>36–38 5–10 5–10 –</td>
<td></td>
</tr>
<tr>
<td>Co-Elinvar</td>
<td>36–39 5–10 9–10 –</td>
<td>Velinvar (V for Cr)</td>
</tr>
<tr>
<td></td>
<td>9–25 20–35 10–12 –</td>
<td>Moelinvar (Mo for Cr)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thungelinvar (W for Cr) and/or additions for Ti, Mn, Si, Al</td>
</tr>
</tbody>
</table>

**Antiferromagnetic**

| Elinvar | MnNiFe 20–28 – – 72–80 | Additions of Fe, Co, Mo, W |
|         | CrFeMn – – 85–95 – 1   | |
|         | MnCu – – – 50–55        | |
they show aging effects (caused by C impurities) and insufficient mechanical strength. Thus, their workability and machinability would be too limited. Therefore, in commercial Invar- and Elinvar-type alloys a broad spectrum of additional elements is used with the purpose of increasing the mechanical strength of the alloys (mainly through precipitation hardening after different heat treatments) and reducing the aging effects as well as the $\Delta E$-effect. Moreover, the weldability and sometimes the corrosion resistance can be improved, if these factors are of importance. Some of the elements added to achieve commercially usable Invar- and Elinvar-type alloys are listed in table 4. The commercial alloys often have six to eight, sometimes even more, different constituents. The spectrum of brand names accompanying this variety is correspondingly broad. Detailed listening of compositions of commercial Invar and Elinvar would go far beyond the scope of this chapter. Although there are many data sheets describing Invar, sometimes the detailed composition of the alloys is kept a companies secret, while sometimes the concentrations given differ considerably in numerical values for the same type of material, or show other contradictory results. Nearly all the literature up to 1965 is listed by McCain and Maringer (1965). Excellent summaries on technical research on and application of Invar and Elinvar can be found in the Honda Memorial Series on Physics and Applications of Invar (1978). Finally, we mention that sometimes the ferromagnetism of Invar and especially Elinvar alloys is an inconvenience for practical applications (e.g., hairsprings for watches, delay lines). Therefore, antiferromagnetic alloys have been developed. Although the spectrum of Invar and Elinvar systems showing antiferromagnetism is wide (cf., table 1), many of the alloys cannot be applied technically, again because of poor machinability, workability, etc. In practical use are antiferromagnetic Cr-rich CrFe alloys (with small additions of Mn), MnCu alloys with additions of Fe, Co, Mo or W (in amounts of 1–10 at%) and ternary FeNiMn alloys. We are, however, convinced that with further understanding of the basic principles, more antiferromagnetic Invar and Elinvar systems suitable for practical purposes will be developed.
3. Magnetic phase diagrams of Invar and Elinvar systems

In this section, we summarize the magnetic phase diagrams of the most important binary and ternary alloy systems showing moment–volume instabilities in general and Invar or Elinvar behavior in special composition ranges (cf., also table 1). Besides the magnetic-transition temperatures, Curie temperatures $T_C$ for ferromagnetic (FM) transitions, Néel temperatures $T_N$ for antiferromagnetic (AF) transitions and $T_f$ for spin glass (SG) or re-entrant spin glass (RSG) like transitions, the diagrams will also contain information about the structural phases occurring in the systems. Conventional nomenclature is used (e.g., $\gamma$ for fcc, $\alpha$ for bcc and $\varepsilon$ for hexagonal structures). In almost all systems presented, the magnetic order has been studied down to $^4$He-temperatures and the magnetic phase-transition lines are, in general, well-known. Concerning structural transitions, the knowledge of martensitic transformation temperatures $M_s$ is very important, since most of the experimental data are achieved on alloys quenched from high temperature (typical 1000–1200°C), where the solubility is correspondingly high. $M_s$-temperatures can be determined with satisfying accuracy from different types of studies, even at low temperatures. Equilibrium solubility lines, necessary to understand the decomposition of metastable alloys, are often less well-known (a famous example is the FeNi diagram, shown in fig. 5, which is still debated).

![Fig. 5. Magnetic phase diagram of Fe$_x$Ni$_{1-x}$ based on experimental data by Crangle and Hallam (1963) and Stamm (1988). Curie temperatures $T_C$ in the $\gamma$-phase and the magnetic moment of the Fe-atoms in the $\alpha$- and $\gamma$-phase $\mu_{Fe}$ as a function of concentration are given. The dashed-dotted lines show the structural equilibrium lines (Kubaschewski 1982) and the martensitic transformation lines (Jones and Pumphrey 1949), respectively. The hatched region indicates a low-temperature mixed magnetic phase as observed in ac susceptibility measurements (Miyazaki et al. 1985).](image-url)
These lines are known with the least accuracy at temperatures below about 500 K. This is due to the fact that the times needed for reaching structural equilibrium in solid-state reactions become extremely long, especially if broad miscibility gaps and extended eutectic (or peritectic) decomposition ranges occur. Therefore, the values for the stability ranges of the respective structural phases in the binary systems given in table 1 and the equilibrium stability lines in the ternary diagrams (section 3.2) have to be regarded with some care.

It was believed for a long time that the Invar effect is bound to the occurrence of a $\gamma - \alpha$ transition and a deviation of the magnetic moment $\mu$ from the Slater–Pauling curve, simultaneously observed on approach to the instability limit. Although the latter condition was put into doubt, because ordered FePt alloys around the composition Fe$_3$Pt (Kussmann and von Rittberg 1950) did not show any weakening of the moment, we shall, in the following diagrams, give the values for the average magnetic moments $\mu$ as a function of composition as well, if data are available from the literature.

3.1. Phase diagrams of binary systems

3.1.1. Fe–Ni system

Figure 5 shows the magnetic phase diagram of the archetypical Invar system Fe$_x$Ni$_{1-x}$. Data were originally published by Crangle and Hallam (1963) but they have repeatedly been verified since then (see e.g., Stamm 1988). One can see that on approach to the $\gamma - \alpha$ phase-transition there is the well-known strong downward deviation of the moment $\mu$ from the Slater–Pauling curve, accompanied by a decrease in the Curie temperature $T_C$. The dashed-dotted lines in fig. 5 give martensitic transformation temperatures $M_s$ as a function of concentration as determined by Jones and Pumphrey (1949) by quenching from high temperatures. The lines represent temperatures corresponding to 10 and 90% martensitic transformation, respectively. The equilibrium phase-transition lines in FeNi are still debated in this composition region (Kubaschewski 1982) and the question about the existence of an ordered Fe$_3$Ni phase is still unanswered. Due to the structural mixing, the magnetic ground state of the alloys around the $\gamma - \alpha$ transition region is also inhomogeneous. The presence of RSG-like properties has been proposed by Miyazaki et al. (1985), the RSG-region being indicated in fig. 5 by the hatched region. As shown in our own work (Zähres et al. 1988) antiferromagnetic $\gamma$-Fe precipitations in a ferromagnetic Fe$_{65}$Ni$_{35}$ $\gamma$-type matrix probably describe the situation better. For the Invar effect in this system, these magnetic inhomogeneities are not of much relevance.

3.1.2. Fe–Pt system

Figure 6 shows the magnetic phase diagram of Fe$_x$Pt$_{1-x}$ in the concentration range 0.55 $\leq$ $x$ $\leq$ 0.95 around the concentration of the Fe$_3$Pt-phase with Cu$_3$Au (L1$_2$) superstructure. Values of the Curie temperatures in the ordered ($T_C^o$) and disordered state ($T_C^d$) as well as the magnetic moment $\mu_F$ as a function of the Fe-concentration have been determined many times. We show very reliable data of Sumiyama et al. (1978). The structural equilibrium lines of Fe$_x$Pt$_{1-x}$ are only
known inaccurately (Hansen and Anderko 1958). However, martensitic $\gamma-\alpha$ transformations indicated by the dashed-dotted lines in fig. 6 occur on cooling, both in the disordered and in the ordered state.

FePt alloys show Invar properties in the disordered as well as the ordered state, but no deviations of the Fe moment from the Slater–Pauling curve on approach to the $\gamma-\alpha$ transition, and no mixed magnetic state at low $T$ (cf., fig. 6). This fact, first realized by Kussman and von Rittberg (1950), for a long time gave this system a somewhat unique position in the discussion about the origin of the Invar effect, until other Invar systems with similar properties, like Fe$_x$Pd$_{1-x}$ and amorphous Fe$_x$B$_{1-x}$, were discovered. We will discuss this in more detail below.

3.1.3. Fe–Pd system

Invar anomalies in the thermal expansion near 30 at% Pd in Fe were first investigated by Kussman and Jessen (1962). They reported that the thermal expansion coefficient of Fe$_{1-x}$Pd$_x$ alloys quenched from the high-temperature $\gamma$-phase shows a minimum around $x = 3.0$. Figure 7 gives (dashed-dotted lines) the high-temperature part of the structural equilibrium phase diagram as established by Raub et al. (1963). Obviously, an ordered Fe$_3$Pd phase does not exist in this system, in contrast to FePt (cf., fig. 6).

According to the data by Raub et al., FePd alloys in the Invar range consist of two phases ($\alpha + $FePd) when in equilibrium. Thus, quenching is a necessary condition to prevent phase separation. On the other hand, quenching from the
γ-range leads to martensite at low temperatures. This has been studied in detail by Matsui et al. (1980a), who determined the position of the $M_s$-line (see fig. 7) and showed that on lowering the Pd-concentration, other structural transitions occur in FePd, an fct $γ'$-phase, a mixed region $α − γ'$, and a bcc $α$-phase below 28 at% Pd (for $T = 0$ K).

The same group (Matsui et al. 1980b) also determined the concentration dependence of the Curie temperatures in the $γ$-phase (open dots in fig. 7) as well as the concentration dependence of the average magnetic moment $\bar{\mu}$ (crosses in fig. 7). While their data on $T_C$ agree well with earlier results by Fujimori and Saito (1965) (solid dots in fig. 7), there is a discrepancy in the $\bar{\mu}(x)$-dependence for $x \leq 0.3$, where Fujimori and Saito (1965) found a deviation of the moment from the Slater–Pauling curve (data not shown in fig. 7). This was, however, obviously due to metallurgical problems. Later investigations by Matsui et al. (1983) confirmed that FePd – like FePt – does not show a decrease in magnetic moment near the $γ−α$ transition in the Invar range. This demonstrates the importance of FePd in the search for the basic understanding of the Invar effect.

### 3.1.4. Fe–Mn system

An interesting alloy system, showing fcc structure in a wide range of composition but only antiferromagnetic order, is FeMn. The magnetic phase diagram is shown in fig. 8. Between 20 and about 60 at% Mn in the $γ$-range the Néel temperatures
rise from 350 to about 520 K as confirmed by different authors (Ishikawa and Endoh 1967, Stamm 1988). The spin structure is noncollinear (Endoh and Ishikawa 1971) but isotropic, as indicated in the inset to fig. 8. On the Fe-rich side there is a steeply decreasing \( \alpha - \gamma \) transition line in the concentration range up to 10 at\% Mn (Schumann 1967). Alloys with higher Mn concentrations, i.e., those in the \( \gamma \)-range, undergo a martensitic transformation at lower temperatures into \( \varepsilon \)-martensite with hexagonal lattice structure. This has been confirmed by Mössbauer measurements (Trichter et al. 1978) and TEM investigations (Gartstein and Rabinkin 1979). The latter authors also showed that \( \varepsilon \)-martensitic needles are present up to about 50 at\% Mn, with the volume fraction of the needles in the rest-austenite being almost temperature and concentration independent. Their findings were supported in recent magnetization measurements by Stamm (1988) on \( \text{Fe}_{1-x}\text{Mn}_x \), with \( 0.26 \leq x \leq 0.59 \), who observed SG-like splittings between the field-cooled (FC) and zero-field cooled (ZFC) susceptibility curves at temperatures indicated by the full dots in fig. 8. The magnetic ground state of \( \gamma \)-FeMn alloys is thus inhomogeneous due to the structural inhomogeneity. It remains an open question, whether the low-lying \( \gamma - \varepsilon \) transitions are accompanied by a transition from the noncollinear spin structure at high temperatures, into a collinear spin structure at low temperatures because of the tetragonal distortion of the lattice occurring simultaneously.

In the range \( 0.53 \leq x \leq 0.69 \), the \( \text{Fe}_{1-x}\text{Mn}_x \) system shows a \( \gamma - \alpha_{\text{Mn}} \) two-phase range, and for \( x \geq 0.69 \) up to 100\% Mn there occurs an \( \alpha_{\text{Mn}} \)-phase, which also
orders antiferromagnetically. The Néel temperatures shown in fig. 8 (crosses) have been determined by Nakai et al. (1986).

3.1.5. Ni–Mn system
In contrast to the FeMn system, the system $\text{Ni}_x\text{Mn}_{1-x}$ has a wider $\gamma$-range, and shows a broad spectrum of magnetic order, ferromagnetism on the Ni-rich side accompanied by RSG- and pure SG-behavior, ferromagnetism in the middle of the diagram around the ordered $\text{L}_{10}$ phase of NiMn, and antiferromagnetism on the Mn-rich side. The magnetic phase diagram, which has been subject of many investigations, especially on the Ni-rich side, is shown in fig. 9. The Curie temperatures $T_C^d$ of the disordered alloys decrease from 632 K for pure Ni to about 100 K at 24 at% Mn (Tange et al. 1978), where a pure SG phase starts to occur. There is also a reentrant SG like phase (hatched region in fig. 9). Data for the alloys in the 20–30 at% Mn range are results from magnetization measurements by Kouvel and co-workers (full dots in fig. 9) (see Abdul-Razzaq and Kouvel 1987 and references therein), and neutron scattering results by Hennion et al. (1984) (plus signs in fig. 9). The decrease of $T_C^d$ with rising Mn concentration is accompanied by a deviation of the average magnetic moment $\mu$ from the

![Fig. 9. Phase diagram of $\text{Mn}_{1-x}\text{Ni}_x$. On the Ni-rich side, Curie temperatures (full squares) and the average magnetic moment (open squares) have been determined by Tange et al. (1978). Other transition temperatures, especially for the spin-glass phase, are from Hennion et al. (1984) (plus signs) and Abdul-Razzaq and Kouvel (1987) (solid dots). Curie temperatures in the ordered alloys $T_C^o$ (crosses) are from Kaya and Kussman (1931). Note that on the Mn-rich side the system orders antiferromagnetically. $T_N$ values (open dots) are due to Honda et al. (1976). Structural transition lines (dashed-dotted) are also due to these authors.](image-url)
Slater–Pauling curve, shown by the dashed curve (open squares) in fig. 9 (Tange et al. 1978). This deviation and the occurrence of a metamagnetic behavior in NiMn around the composition Ni$_3$Mn has also been widely studied theoretically in different types of models (see, e.g., Jo 1980, Kakehashi 1984 and references therein). The scattering of the data for $T_C^d$ and $T_r$, as well as the discrepancies between experimental and theoretical results to our feeling originate from the fact that in the range around ordered Ni$_3$Mn (the existence of that phase has not been proven yet), there are also high-temperature PM–FM transitions possible in annealed, ordered alloys. This has been known since a long time (Kaya and Kussmann 1931, Köster and Rauscher 1948). Curie temperatures $T_C^o$ are shown by the crosses in fig. 9. Quenching of NiMn alloys with Mn concentrations exceeding 20 at% with different quenching rates therefore leads to different magnetic short-range order (SRO) in the disordered state, and to unreproducible magnetic data. Obviously, complete disorder can not be achieved experimentally.

On the Mn-rich side of the NiMn system, the structural phase transformation lines are not very well established at high temperatures. There is probably a eutectic decomposition of $\beta_{\text{Mn}}$ into $\alpha_{\text{Mn}}$ and a $\gamma$-phase at 820 K, the $\gamma$-phase being stable down to low temperatures above about 22 at% Ni. The $\gamma$-type alloys have antiferromagnetic order. $T_N$ values shown in fig. 9 (open dots) are from Honda et al. (1976). Alloys with 22–27 at% Ni show Elinvar properties as confirmed by these authors. Alloys with Ni concentrations smaller than 22 at% (at $T = 0$ K) undergo complicated structural transitions. There are regions with fct structure with $c/a > 1$, fc orthorhombic structure, and fct structures with $c/a \approx 1$ as seen from the dashed-dotted lines in fig. 9 (Honda et al. 1976).

### 3.1.6. Co–Mn system

This system is complicated by the existence of the two allotropic forms of Co, a close packed hexagonal $\varepsilon$-form, stable at temperatures below 417 ± 10°C, and a cubic $\gamma$-form, stable at higher temperatures up to the melting point (1495°C), as well as the four allotropic forms of Mn. A reliable structural phase diagram has been published by Tsioplakis and Gödecke (1971). We show in fig. 10 the magnetic phase diagram in the range from pure Co to the phase CoMn. The Curie temperatures in the $\gamma$-range decrease sharply with increasing Mn-concentration [see fig. 10; full dots: H. Matsumoto et al. (1969); open dots: Matsui et al. (1970); open triangles: Bendick and Pepperhoff (1979)] and ferromagnetism vanishes around 35 at% Mn. The average magnetic moment $\bar{\mu}$ decreases linearly with increasing Mn content as reported by Matsui et al. (1970) (open dots) and Cable (1982) (solid squares), and vanishes also at 35 at% Mn. In the range $0.32 \leq x \leq 0.40$ mixed magnetic behavior is observed (Rhiger et al. 1980; crosses in the figure) and the magnetic SRO is of complicated nature in that region, leading to contradictory results. A pure SG phase very likely does not exist. Pauli paramagnetic behavior was reported for $x = 0.39$ (Rhiger et al. 1980), antiferromagnetism for alloys with $x = 0.36$ and 0.37 (Matsui et al. 1970). Dorofeyev et al. (1988), who recently reinvestigated the Co$_{1-x}$Mn$_x$ magnetic phase diagram also found
some RSG like transition points in the FM alloys at temperatures around 100 K (see open squares in fig. 10). In our feeling, all these discrepancies stem from the fact that the $\gamma-\epsilon$ structural transition line is crossed, when quenching alloys from the high temperature $\gamma$-range to lower temperatures, thus causing unrepeatable SRO effects in the composition range in question.

When approaching the composition CoMn ($e/a = 8$, like pure Fe) the system becomes antiferromagnetic. Although the L1$_0$ superstructure probably does not exist, Co$_{1-x}$Mn$_x$ alloys with $x = 0.48$ and $x = 0.5$ show AF long-range order (see plus signs in fig. 10) as confirmed by neutron scattering investigations on powdered and single-crystalline samples by Adachi et al. (1973).
3.1.7. Co–Fe and Co–Ni systems

Figure 11 shows the magnetic phase diagrams for Co$_{1-x}$Ni$_x$ (right-hand part) and the Co-rich side of the CoFe system (left-hand part), both diagrams have been taken from Bendick et al. (1979). The CoNi system forms a complete series of solid solutions with γ-structure, and the Curie temperatures decrease continuously from $T_C = 1390$ K (Co) to $T_C = 632$ K (Ni). In CoFe, the Curie temperatures decrease on addition of Fe, the high-temperature γ-range, however, has a limit of about 25 at% Fe. In both systems, martensitic transformations into the ε-phase are found close to pure Co (see dashed-dotted lines in fig. 11) on quenching as well as heating.

![Figure 11. Magnetic phase diagram of Co$_{1-x}$Ni$_x$ and part of the diagram of Co$_{1-x}$Fe$_x$ as determined by Bendick et al. (1979). Some structural-transition lines, especially into ε-martensite are also given (dashed-dotted lines).](image)

3.1.8. Cr–Fe system

A well-studied bcc alloy system showing moment–volume instabilities and Invar properties in a wide range of composition is Fe$_{1-x}$Cr$_x$. The magnetic phase diagram is shown in fig. 12. It has been established from data by Burke et al. (1983) (solid dots for $T_C$, $T_N$) and from Burke and Rainford (1978) (dashed curve for $\tilde{\mu}$) in the range $0.65 \leq x \leq 1$. $T_C$ values on the Fe-rich side (triangles) are due to Fukusaka et al. (1986), and the open dots show the values of Aldred (1976) for the concentration dependence of the average moment $\tilde{\mu}$ (open dots) in the range $0 \leq x \leq 0.7$. As one can see from the diagram, there is a continuous decrease of $T_C$ and $\tilde{\mu}$ with increasing Cr concentration, a transition region with RSG and SG order, and then AF-order on the Cr-rich side. Here, we neglect the complications and extra transition lines on the Cr-side caused by the occurrence of incommensurate (up to about 6 at% Fe) and commensurate spin-density waves (CSDW) at
higher Fe-concentrations in Cr. The structural phase diagram of FeCr is also well-investigated. The exceptional feature is a decomposition of the high-temperature $\alpha$-phase at 440±20°C (Rivlin and Raynor 1980) or 570°C (Fukusaka et al. 1986), so that in low-temperature equilibrium the alloys in the whole system would decompose into Fe- and Cr-rich components, respectively.

3.1.9. Cr–Mn system
Another bcc-type alloy system is $\text{Cr}_{1-x}\text{Mn}_x$, where the $\alpha$-phase is stable up to $x = 0.6$. The magnetic order of the alloys is solely antiferromagnetic, very small Mn-concentrations ($x \leq 0.01$) and problems due to incommensurate spin-density waves disregarded. The Néel temperatures rise sharply from $T_N = 312$ K for pure Cr to $T_N = 750$ K for Cr with addition of 2 at% Mn. Above this concentration, $T_N$ is almost constant with rising Mn concentration up to the stability limit of the $\alpha$-phase (see, e.g., Maki and Adachi 1979).
3.2. Phase diagrams of ternary systems

3.2.1. Fe–Ni–Cr system
Alloys in the γ-range of FeNiCr are widely used as commercial Elinvar (see crosses in fig. 13) and are even more important as austenitic stainless steels. They also show Invar properties (Acet et al. 1987, 1988). Therefore, the system has been extensively studied in structural and magnetic investigations. The magnetic phase diagram is shown in fig. 13. Data for the γ-range stability line (at room temperature) and Curie temperatures projected into the zero-Kelvin plane are mainly taken from papers by Menshikov et al. (1979, 1982), who investigated the total γ-area by neutron-scattering and magnetization measurements. While these data in the purely FM range agree well with other results in the literature, the antiferromagnetic, Fe-rich side close to the γ–α transition is a problematic range, and contradictory results are reported. To date, it is almost certain that a homogeneous long-range ordered antiferromagnetic phase in the outside corner of the γ-range never develops (Ishikawa et al. 1975, Takzey et al. 1981), although other authors claim AF order with low $T_N$ (30–60 K) to occur (Warnes and King 1976, Majumdar and von Blanckenhagen 1984). The problem is analogous to that in binary systems – like, e.g., FeNi. Close to the γ–α phase boundaries, the exact positions of the martensitic transformation lines $M_s$ down to very low temperatures are not known with sufficient accuracy. Moreover, $M_s$ depends critically on interstitial impurities like C or N. Very likely the $M_s$-line at 0 K (see dashed line in fig. 13) lies inside the region with AF and FM SRO, while $M_s$ for 300 K definitely lies outside the stability range of the γ-phase.

Fig. 13. Ternary magnetic phase diagram of FeNiCr in the γ-range (Menshikov et al. 1979, 1982, Majumdar and von Blanckenhagen 1984). The full lines show contours of constant Curie temperatures projected into the zero-Kelvin plane. The RSG area is shown hatched, the pure SG area dotted. On the Fe corner within the γ-range, a pure antiferromagnetic long-range order never develops (Ishikawa et al. 1975, Takzey et al. 1981) because of the occurrence of a martensitic transformation [$M_s$-lines from Warnes and King (1976)]. The crosses mark commercial Invar and Elinvar compositions.
Along the rim of the FM-range, FeNiCr alloys show RSG behavior at low temperatures (see hatched area in fig. 13) with a pure SG region adjacent (dotted area in fig. 13). This has been supported by our recent investigations of the frequency dependence of the AC susceptibility on Fe$_{80-x}$Ni$_x$Cr$_{20}$ alloys with $14 \leq x \leq 35$ at% (Uffelmann 1987).

### 3.2.2. Fe–Ni–Mn system

Ferromagnetic FeNi Invar alloys with small additions of Mn and AF Elinvar alloys of MnNi with small additions of Fe, both used commercially, can be found in the ternary system of FeNiMn. The magnetic phase diagram is shown in fig. 14. The system exhibits a wide range of γ-stability, with exceptions at the corners of Fe ($\alpha_{Fe}$ and low-temperature $\epsilon$-martensite), Mn ($\alpha_{Mn}$), and around the ordered phase of NiMn. Moment–volume instabilities are found throughout the whole γ-range. The magnetic transition lines, Néel temperatures $T_N$ for the AF Fe–Mn-rich side, and Curie temperatures $T_C$ for the FM Fe–Ni-rich side projected into the 0 K-plane are given in the figure. The system has been intensively studied and the data shown are compiled from the literature (Shiga 1967, Menshikov et al. 1976, 1981, Ettwig and Pepperhoff 1974). Concerning the Invar behavior, alloys along the composition Fe$_{80-x}$Ni$_x$Mn$_{50-x}$ have been recently reinvestigated by us in

![Fig. 14. Magnetic phase diagram of the ternary system FeNiMn in the fcc γ-phase, compiled from different data in the literature (Shiga 1967, Menshikov et al. 1976, 1981, Ettwig and Pepperhoff 1974, Stamm 1988, Acet et al. 1987). Contour lines for constant Néel temperatures $T_N$ in the antiferromagnetic phase and Curie temperatures $T_C$ in the ferromagnetic phase are shown. The dotted region marks a pure spin-glass phase separating the AF and FM regions. The hatched region gives the area of a re-entrant spin-glass phase, which occurs below the FM ordering. Crosses mark commercial Invar and Elinvar compositions.](image-url)
detail (Acet et al. 1988). Transition temperatures from the AF and FM side fall into a deep valley, along which RSG behavior (hatched area in fig. 14) and a pure SG phase (dotted in fig. 14) are found. Compositions of the commercial alloys are denoted by crosses.

3.2.3. Fe–Ni–Co system

The magnetic phase diagram of FeNiCo is shown in fig. 15. It is based on constitutional data taken from the Cobalt Monograph (1960) and early magnetic investigations by Masumoto (1931). The system shows a wide range of γ-stability, a hexagonal ε-phase near pure Co and a narrow α-range along the Fe–Co side. Between the α- and γ-ranges lies a broad region of α + γ mixtures. Some of the high to low temperatures $M_s$ transition lines (dashed-dotted) are given in fig. 15. The magnetic order is solely ferromagnetic throughout the whole diagram, with high Curie temperatures, as can be read from the respective projection lines in the figure. The projected $T_C$-lines end at the respective $M_s$-lines in the α + γ range. Most of these $M_s$-lines are omitted for clearness in fig. 15, but they, in principle, are running parallel to the 800 K line. The FeNiCo diagram is of practical importance. The commercial Invar compositions for ‘Super-Invar’ (around 0–18 at% Co) as well as certain FeNi Invars are indicated by the crosses. All these compositions are found close to the γ–α instability limit. FeNiCo alloys of other compositions are also of practical importance, e.g., as high-damping materials, and, with the addition of Cr, as high-temperature–high-strength super alloys.

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Fig. 15. Magnetic phase diagram of FeNiCo after Bozorth (1950) based on magnetic data by Masumoto et al. (1931) and structural data taken from the Cobalt Monograph (1960). Note the wide range of γ-miscibility in this system and the absence of any AF, RSG or SG order.
3.2.4. Fe–Co–Mn system

The structural equilibrium phase diagram of this system has been established by Köster and Schmidt (1933). As can be seen from fig. 16, there is a relatively broad range of fcc, γ-structure at room temperature (dashed-dotted lines), though none of the constituents is stable in the γ-phase at this temperature. The magnetic data shown in fig. 16 originate from careful investigations by Adachi et al. (1971) and Matsui et al. (1973) and a recent study by Dorofeyev et al. (1988), the latter of the composition Co$_{1-x}$(FeMn)$_x$. The system also shows a transition from ferromagnetic order with very high Curie temperatures on the Co-rich corner, through mixed magnetic RSG like order (hatched area in fig. 16), pure SG behavior (dotted area) to AF order on the FeMn side. In comparison to the binary CoMn system (cf. fig. 10), which probably does not show a SG phase, a broad SG region opens up on the addition of Fe into CoMn.

In the FM alloys left hand to this SG range and close to the α–γ transition line ($e/a = 8.4–8.5$), Invar-like magnetovolume effects have been observed, while a binary Co$_{70}$Mn$_{30}$ alloy close to the γ–ε transition line (with the same ratio $e/a = 8.4$) did not show this effect (Matsui et al. 1973). This was not understood at the time it was detected, but will become clear on the basis of modern band-structure calculations, as we shall see later. We finally mention that the extension of the low-temperature ε-martensite field (the ε-martensite occurs on quenching of the γ-phase alloys) is not well-investigated in the ternary FeCoMn

![Fig. 16. Magnetic phase diagram of FeCoMn. The data originate from Adachi et al. (1971), Matsui et al. (1973) and Dorofeyev et al. (1988). Characteristic for this system is the deep 'valley' between the FM and the AF range, where a pure SG phase (dotted area) is observed. Structural-transition lines at room temperature (dashed-dotted) are due to Köster and Schmidt (1933). Note the 'opening up' of the SG area on approach of the γ–α transition region.](image)
system. The phase-transition line drawn in fig. 16 \((\gamma + (e))\) is therefore tentative and roughly valid for \(M_s = 300\) K. The \(\gamma + (e)\) field will stretch more into the direction of Mn, if alloys are quenched to lower temperatures.

3.2.5. \textit{Ni–Co–Mn} system

Figure 17 shows the magnetic phase diagram of NiCoMn. The system has a wide range of \(\gamma\)-stability, and shows ferromagnetic order with high \(T_C\)-values on the CoNi side, which decrease drastically on addition of Mn. Along the line from \(\text{Co}_{36}\text{Mn}_{64}\) to \(\text{Ni}_{75}\text{Mn}_{25}\), there is a deep valley of SG order with low transition temperatures \((T_f = 50–80\) K). To the right-hand side of the valley antiferromagnetic order occurs, with \(T_N\) values rising to more than 400 K with increasing Mn concentration. On either side of the SG valley there are regions of mixed magnetic behavior (hatched regions in fig. 17), which have RSG character on the FM side, and ferro–antiferromagnetism coexisting on the AF side. The structural part of the diagram is due to work by Köster and Rittner (1954). In the Co corner there is \(e\)-order with structural transition temperatures lying below the respective Curie temperatures. At the Mn corner and along the Mn–Ni side the lattice structure is more complex due to the allotropy of Mn. According to Köster and Rittner (1954), about 3 at\% Co can be dissolved in ordered NiMn. However, the

![Fig. 17. Magnetic phase diagram of the ternary system NiCoMn (Cobalt Monograph 1960). Solid lines show constant Curie and Néel temperature contours projected into the zero-Kelvin plane. Note the deep lying, narrow spin-glass region (dotted area), which runs across the diagram, separating the FM from the AF region. Hatched areas indicate re-entrant spin-glass phases observed in the FM as well as the AF range. Structural-transition lines (at 20°C) (dashed-dotted) have been determined by Köster and Rittner (1954). Note the small solubility of Co in ordered NiMn, in contrast to the extended range of \((\gamma + \text{NiMn})\) phase mixtures.](image-url)
contour of the phase boundary \((\gamma + \text{NiMn}) - \gamma\) boundary at room temperature (see dashed-dotted line in fig. 17) extends far into the \(\gamma\)-region and phase mixtures occur even in alloys quenched from 1000°C.

3.2.6. Co–Fe–Cr system

CoFeCr alloys are of importance for technical applications, since the FM fcc alloys ‘Stainless-Invar’ and ‘Co-Elinvar’ (cf., table 4) are found in this system. The structural phase diagram has a very simple form at high temperatures as seen in the inset to fig. 18 (Rideout et al. 1951). There are two wide ranges of solid solutions, with \(\gamma\)-structure on the Co–Fe side and \(\alpha\)-structure on the Cr-rich corner. On lowering of the temperature, the diagram gets very complicated. Alloys of composition within the area labeled A in the inset to fig. 18 transform completely into bcc \(\alpha\)-structure on quenching, while alloys of composition within area B decompose on quenching, mostly into the hexagonal \(\varepsilon\)-phase (and \(\varepsilon-\sigma\) mixtures), and only a small \(\gamma\)-region is left. This \(\gamma\)-region is shown by the dotted area in fig. 18. The respective composition lines at RT determined by Köster and Hofmann (1959) are shown by the dashed-dotted lines.

The structural part of the CoFeCr diagram reveals that the Stainless-Invar alloys with compositions \((\text{Fe}_{1-x}\text{Co}_x)_{90}\text{Cr}_{10}\) and \(0.52 \leq x \leq 0.54\) (Masumoto 1934), just lie within the narrow right-hand end of the \(\gamma\)-stability range, very close to the boundaries of the \(\alpha\)- and \(\varepsilon\)-phase. This means that results concerning the magnetic properties of alloys in the Stainless-Invar range have to be regarded with care. Occurrence of phase mixtures is the immediate consequence of slight errors in the Cr concentration. This is less critical for Co-Elinvar, since for 58–
60 at% Co and 9–10 at% Cr the γ-phase is a little wider. We remark that on addition of Ni in the quaternary diagram CoFeCrNi (cf., fig. 4) the γ-area opens up.

Curie temperatures are hardly known for the γ-range. Some $T_C = \text{const.}$-lines projected into the basal plane are shown in fig. 18 (Masumoto 1934).

4. Fundamental properties of Invar and Elinvar systems

Following the listing in table 2, we will present in this section the principal behavior of the physical properties of Invar (and Elinvar) systems as a function of external parameters like temperature, magnetic field, or pressure. We will restrict ourselves to the presentation of selected data on specific systems, which are relevant for the general understanding of the Invar effect within modern band calculations presented below. This is also necessary for the sake of clearness, and in order not to confuse the reader with the overwhelming mass of data available for all the systems presented in section 3. These are well summarized in the Honda Memorial Series on the Invar problem (1978) up to the year 1978. Thus, we will mainly outline the new insights gained since then.

4.1. Thermal expansion

Doubtlessly, the anomaly in the thermal expansion is the most characteristic feature of Invar. For ferromagnetic alloys, the principal behavior of the length change with temperature and the temperature dependence of its derivative – the expansion coefficient $\alpha(T)$ – have already been shown in figs. 1a and 1b. Less well-known is the dependence of $\alpha$ on the temperature in antiferromagnetic Invar. To exhibit the differences, we have measured the thermal expansion on systems, where a transition from FM to AF order through a SG phase is possible by change of the concentration of one of the constituents (Acet et al. 1988a). Together with data from the literature, this leads to a sizeable set of results that enables us to observe some general features of magnetovolume effects in FM, SG and AF systems (Acet et al. 1988a).

Figure 19 shows, as an example, $\alpha(T)$ in Fe$_{65}$Ni$_x$Mn$_{35-x}$ (Acet et al. 1988a, Hayase et al. 1971). In this system, a continuous transition from FM (Fe$_{65}$Ni$_{35}$) through a SG (Fe$_{65}$Ni$_{25}$Mn$_{10}$) to AF (Fe$_{65}$Mn$_{35}$) is obtained by a variation of the Ni content (cf., magnetic phase diagram in the inset of fig. 19b and also fig. 14). As seen in fig. 19a, the FM alloys show positive magnetovolume effects with respect to the calculated Grüneisen curve. One might expect the SG alloy to represent the nonmagnetic Grüneisen behavior, but in fact it does not, since it is paramagnetic. It only follows the calculated Grüneisen curve in the low-temperature range. Note that there are substantial contributions to $\alpha(T)$ above the respective Curie temperatures in the FM alloys. As seen from fig. 19b, the AF alloys show positive magnetovolume effects like the FM alloys to temperatures above $T_N$, but then, in the PM range ($T \gg T_N$), their $\alpha(T)$ curves cross the
Fig. 19. Thermal expansion coefficient $\alpha$ as a function of temperature for different ferromagnetic (a), antiferromagnetic (b), pure spin-glass (SG) and re-entrant spin-glass (RSG) alloys of the system Fe$_{65}$Ni$_x$Mn$_{35-x}$ [after Hayase et al. (1971) and own data, Acet et al. (1988a)]. The Grüneisen curve is fitted to the data of the SG alloy ($x = 25$ at% Ni) at low temperatures. The inset shows the magnetic phase diagram, the arrows mark the respective concentrations, for which the $\alpha(T)$ curves are given.

Grüneisen curve, show an additional maximum and approach it from above for higher temperatures.

This is better revealed in fig. 20, where $\alpha(T)$ for binary CoMn alloys is shown in the temperature range up to 1100 K (Pepperhoff 1989). Note the pronounced maxima and the decrease in $\alpha(T)$ in the high-temperature PM range. In relation to the discussion in section 3.1.6 we also mention here that in the FM CoMn sample with $x = 32.5$ at% Mn ($T_C \approx 150$ K) a positive magnetovolume effect is indeed absent around $T_C$. However, this alloy might not be a FM but superparamagnetic according to the phase diagram in fig. 10, so that the question for the absence of the Invar effect on approach to the $\gamma-\varepsilon$ structural phase transition line has to be left open, until further data are available.

The general $\alpha(T)$ behavior in ferromagnetic and antiferromagnetic Invar systems can be summarized in the following way:

(i) $\alpha(T)$ curves for ferromagnetic alloys always lie below the respective
Grüneisen curve and show positive magnetovolume effects, regardless of the temperature. FM Alloys also have substantial magnetovolume effects above the respective Curie temperatures in the paramagnetic range which vanish, however, gradually for very high temperatures.

(ii) Antiferromagnetic Invar alloys, in principle, show the same behavior, positive magnetovolume effects (although less in absolute values as compared to FM Invar) below and around $T_N$. Yet, in the PM range for $T > T_N$, their $\alpha(T)$ curves cross the respective Grüneisen curves and show distinct maxima, calling for the reappearance of a magnetovolume effect. This is shown schematically in fig. 21, where the relative volume change of ferromagnetic (FM) (full curve, cf., fig. 1a) and antiferromagnetic (AF) Invar (dashed curve) is given in comparison to a nonmagnetic (NM) Grüneisen-like reference.

(iii) Pure SG alloys expand Grüneisen-like up to temperatures roughly five times their freezing temperature $T_f$, but then – like the AF alloys – show positive magnetovolume instabilities at high temperatures in the PM range and approach the Grüneisen curve from above for $T$ going to infinity.

The principal change of the expansion coefficient $\alpha$ with impurity concentration for FeNi at room temperature (RT) has been presented in fig. 2. In fig. 22 we have plotted $\alpha_{RT}$ versus the electron per atom ratio $e/a$ for a series of different Invar systems. Data are taken from the literature (Acet et al. 1988a, Honda Memorial Series 1978). A deep minimum with $\alpha_{RT} = 0$ (or even negative values in FePt) occurs in the range $e/a = 8.5$–8.7 for certain binary and ternary systems (Invar effect) which are all ferromagnetic. Note that in this $e/a$ range the
Fig. 21. Schematic representation of the volume change with temperature in ferromagnetic (FM) and antiferromagnetic (AF) Invar in comparison to a non-magnetic (NM) Grüneisen alloy.

Fig. 22. Thermal expansion coefficient at room temperature $\alpha_{RT}$, as a function of the electron concentration $e/a$, for different Invar systems as compiled from the literature (Acet et al. 1988a, Honda Memorial Series 1978). Arrows on the abcissa mark the martensitic transition temperatures $M_s$ at room temperature for the respective systems. Note the occurrence of two minima in $\alpha_{RT}(e/a)$ in the ferromagnetic range $e/a = 8.5-8.7$ and the antiferromagnetic range around $e/a = 7.6$. In the spin-glass range ($e/a \approx 8.3$), $\alpha_{RT}$ for the respective Invar alloys is larger than $\alpha_{RT}$ of pure copper (see arrow).
respective systems are all close to the $\gamma-\alpha$ structural transition. The respective martensitic transformation temperatures at RT, $M_s^{RT}$, are given by the arrows in fig. 22. For $e/a > 9$, $\alpha_{RT}$ approaches a constant value of about $12 \times 10^{-6}$ K$^{-1}$. Isothermes of $\alpha(e/a)$ for higher (lower) temperatures in principles look similar. The minimum stays in the range $e/a = 8.5-8.7$, the respective curves are just shifted upwards (downwards). A second salient feature of fig. 22 is the maximum in $\alpha_{RT}$ at $e/a \approx 8.3-8.4$, i.e., at the transition from FM to AF order in the SG range (exception: Fe$_{80-x}$Ni$_x$Cr$_{20}$, SG phase for $x = 20$, which corresponds to $e/a = 8.0$). Note that here, $\alpha_{RT}$ reaches values as high as $19 \times 10^{-6}$ K$^{-1}$, higher than the values of pure copper at RT. These alloys are thus used as active components in bi-metals together with low $\alpha_{RT}$ Invar. Finally, we see in fig. 22 that a second minimum in $\alpha_{RT}(e/a)$ is reached in the AF range at $e/a = 7.5-7.6$, which is, however, not as deep as on the FM side of the diagram.

For bcc alloys (Cr-Fe, Cr-Mn) minimum values of $\alpha = 0$ are reached around $e/a = 6.5$, yet, not for RT but at lower temperatures $T \leq 200$ K, since the transition temperatures of these alloys are so low.

Our presentation shows that for the understanding of the Invar-effect and magnetovolume effects of transition metal alloys in general, the 3d-electron concentration is of relevance. Critical values for low $\alpha$ are the ranges $e/a = 8.5-8.7$ for ferromagnetic alloys, and $e/a = 7.5-7.6$ for antiferromagnetic alloys. This will be supported by the theoretical results as we shall see below (section 6.1 and fig. 50e).

4.2. Volume magnetostriction

The principal behavior of $\omega = \Delta V/V$ as a function of temperature has already been presented above (cf. figs. 1, 2 and 21). The spontaneous volume magnetostriction $\omega_s$ is related to $\alpha_m = \alpha_{\exp} - \alpha_{nm}$, the magnetic contribution to the expansion coefficient, by,

$$\omega_s(T) = 3 \int_{T_1}^{T} \alpha_m \, dT ,$$

where $T_1$ is a reference temperature, for which $\omega_s$ is assumed to vanish.

At this point again the problem of finding the 'correct' non-magnetic reference from first principles arises, since for the determination of the magnetic part $\omega_s(T)$ the knowledge of $\omega_{nm}(T)$ or $\alpha_{nm}(T)$ is required. The usual approach (as indicated) is to use thermodynamics, i.e., a Grüneisen relation,

$$\alpha_{nm}(T) = \frac{\kappa \gamma}{3V} C_v(T) ,$$

where $\kappa$ is the compressibility, $\gamma$ the Grüneisen parameter, $V$ the atomic volume,
and $C_v$ the lattice specific heat at constant volume. Integration of eq. (2) leads to,

$$
\alpha_{nm}(T) = \frac{\kappa \gamma}{V} \int_0^T C_v(T) \, dT.
$$

This approach, however, just 'transfers' the problem, since now the knowledge of
the lattice specific heat of the nm reference $C_v(T)$ is required, which, in principle,
is also unknown. Commonly, in the literature, Debye theory with 'suitable' Debye temperatures is used to evaluate $C_v$, and the term $\kappa \gamma/V$ is determined by
fitting eq. (3) to the slope of the experimentally determined volume (length)
change curves in the 'linear' range above $T_C$ (or $T_N$). This procedure completely
neglects the sizeable contributions to $\omega_{\exp}(T)$ in the paramagnetic range of Invar
systems (see figs. 19 and 20), and especially does not work for antiferromagnetic
Invar (cf., fig. 21), since a linear range in $\omega_{\exp}(T)$ [or $\alpha_{\exp}(T)$] can hardly be
defined for these alloys. Even pure SG alloys (see fig. 19) are not suitable as
reference, because they show volume instabilities in the PM range too. All
absolute values of $\omega_{\exp}$ for Invar are, therefore, burdened with some uncertainty.

However, it is certainly correct to say that the spontaneous volume magneto-
striction $\omega_{\text{so}}$ in ferro- and antiferromagnetic Invar is large and positive as
compared to other magnetic materials. This is seen from fig. 23, where $\omega_{\text{so}}$ as a
function of concentration ($e/a$) is plotted for different fcc Invar systems (Data
from Richter and Pepperhoff 1976, Wassermann 1987, 1989a,b). Maximum values

Fig. 23. Spontaneous volume magnetostriction at zero temperature $\omega_{\text{so}}$ versus electron concentration $e/a$ for different Invar systems with fcc lattice structure [after Richter and Pepperhoff (1976) and Wassermann (1987, 1989a,b)]. Note that $\omega_{\text{so}}$ reaches maximum values in those concentration regions, where $\alpha_{\text{RT}}$ (cf. fig. 22) has minimum values. On the other hand, $\omega_{\text{so}}$ vanishes in the SG range around $e/a = 8.3$, where $\alpha_{\text{RT}}$ reaches maximum values.
of $\omega_{s0} = 1.9 \times 10^{-2}$ are reached on the ferromagnetic side in the FeNi system, but the antiferromagnetic fcc alloys also experience a substantial volume magnetostriction, with maximum values of $\omega_{s0} = 1.2 \times 10^{-2}$ in FeMn. As expected, fig. 23 is a 'mirror image' of fig. 22. In the range where $\alpha_{RT}$ in fig. 22 has minimum values ($e/a = 8.5-8.7$ in the FM-range and $e/a = 7.6-7.7$ in the AF-range), maximum volume magnetostriction $\omega_{s0}$ is reached in fig. 23. Vice versa, in the SG range around $e/a = 8.3$, the spontaneous volume magnetostriction vanishes, while $\alpha_{RT}$ reaches maximum values. In table 5 we summarize values for the spontaneous volume magnetostriction at zero temperature for other Invar systems as taken from the literature. Note that in the cubic Laves phases values of $\omega_{s0}$ are smaller – in $\text{RE}_2\text{Fe}_{17}$ and mixed compounds larger – than in the fcc transition-element alloys. Very large spontaneous volume magnetostrictions are found in the $\text{RE}_2\text{Fe}_{14}\text{B}$ compounds. Due to the complex magnetic microstructure of these compounds this observation is far from being understood. The 'giant' value of $\omega_{s0} \approx 5\%$ in AF YMn$_2$ is doubtful, since its occurrence is coupled to a first-order transition (Nakamura 1983).

Amorphous Invar systems show $\omega_{s0}$ values of the same order of magnitude as the crystalline 3d-alloy systems. Data have been collected by Xianyu et al. (1985). A maximum value of $\omega_{s0} = 2.05 \times 10^{-2}$ is reached in $\alpha$-$\text{Fe}_{85}\text{B}_{15}$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\omega_{s0} \times 10^{-2}$</th>
<th>Compound</th>
<th>$\omega_{s0} \times 10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GdCo$_2$</td>
<td>0.72 [1]</td>
<td>ScFe$_2$</td>
<td>0.55 [2]</td>
</tr>
<tr>
<td>TbCo$_2$</td>
<td>0.68 [1]</td>
<td>TiFe$_2$</td>
<td>0.25 [2]</td>
</tr>
<tr>
<td>DyCo$_2$</td>
<td>0.55 [1]</td>
<td>ZrFe$_2$</td>
<td>1.0 [2]</td>
</tr>
<tr>
<td>HoCo$_2$</td>
<td>0.55 [1]</td>
<td>HfFe</td>
<td>0.8 [2]</td>
</tr>
<tr>
<td>ErCo$_2$</td>
<td>0.47 [1]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>YMn$_2$</td>
<td>5.0 [1]</td>
<td>YFe$_2$</td>
<td>small, negative [2]</td>
</tr>
<tr>
<td>$\text{Y}<em>2\text{Fe}</em>{17}$</td>
<td>1.7 [3]</td>
<td>$\text{Dy}<em>2(\text{Fe}</em>{0.8}\text{Co}<em>{0.2})</em>{17}$</td>
<td>2.25 [4]</td>
</tr>
<tr>
<td>$\text{Lu}<em>2\text{Fe}</em>{17}$</td>
<td>1.5 [3]</td>
<td>$\text{Dy}<em>2(\text{Fe}</em>{0.82}\text{Al}<em>{0.18})</em>{17}$</td>
<td>0.75 [4]</td>
</tr>
<tr>
<td>$\text{Dy}<em>2\text{Fe}</em>{17}$</td>
<td>1.7 [4]</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$\text{RE}_2\text{Fe}_{17}\text{B}$ [5], RE = 

La 2.52 Gd 3.36
Ce 3.21 Tb 3.18
Pr 2.79 Dy 3.51
Nd 2.79 Ho 3.54
Sm 2.73 Er 3.12

References:
4.3. Forced volume magnetostriction and high-field susceptibility

The anomalies in the thermal expansion and volume magnetostriction in Invar alloys originate—as mentioned above—from the instability of their magnetic moments. The size of the moment is sensitive not only to composition and temperature, but also to external magnetic fields. If the field is increased beyond values necessary to reach technical saturation, the volume of a ferromagnetic Invar alloy continues to increase with rising field strength. This phenomenon is called ‘forced volume magnetostriction’, expressed by $\partial \omega / \partial H$, if $\omega$ increases linearly with $H$. By a simple thermodynamic argument (Becker and Döring 1939) $\alpha_{\text{exp}}$ and $\partial \omega / \partial H$ can be related. In Invar, one expects a large positive forced volume magnetostriction since $\alpha_{\text{exp}}$ is small (or negative).

Figure 24 shows $\omega_{\text{exp}}(H)$ at various temperature for Fe–36.4 at% Ni. Data have been determined by Ishio and Takahashi (1985). In the temperature range from 77 to 160 K, $\omega$ increases linearly with $H$, and the forced volume magnetostriction is readily evaluated. However, if $T$ is raised up to the Curie temperature $T_C$ (529 K), the slope of the $\omega(H)$ curves decreases with increasing field, at least in

![Figure 24. Experimentally determined volume expansion $\omega_{\text{exp}}$ as a function of magnetic field $H$ for Fe-36.4 at% Ni at various temperatures (after Ishio and Takahashi 1985). The Curie temperature is $T_C = 529$ K.](image)
the low-field range \(0 \leq H \leq 1\ T\). For \(T > T_C\) in the PM range, opposite behavior is observed. \(\omega(H)\) has increasing slope with increasing field; Ishio and Takahashi (1985) even claim \(\omega \propto H^2\). Thus values of \(\partial \omega / \partial H\) cannot be defined at all for \(T > T_C\). We have recently found (Acet et al. 1988b) the same general behavior of \(\omega(H)\) as in fig. 24 on ferromagnetic \(\text{Fe}_{50}\text{NiMn}_{30-\text{x}}\) alloys in fields up to 6 T. Thus, in the temperature range around \(T_C\), it is not adequate to discuss magnetovolume effects in terms of \(\partial \omega / \partial H\) in Invar.

Unfortunately, the same statement is valid for low temperatures, where, e.g., for ordered and disordered \(\text{Fe}_{72}\text{Pt}_{28}\), values of \(\partial \omega / \partial H \approx 10 \times 10^{-10} \text{ Oe}^{-1}\) have been reported for \(T = 50\ K\) (Sumiyama et al. 1979), while in \(\text{Fe}_{65}\text{Ni}_{35}\) at the same temperature \(\partial \omega / \partial H = 75 \times 10^{-10} \text{ Oe}^{-1}\) (Ishio and Takahashi 1985). Moreover, for \(T \leq 20\ K\), \(\partial \omega / \partial H\) in \(\text{Fe}_{65}\text{Ni}_{35}\) suddenly drops and becomes time dependent in the low-temperature range. The same behavior of \((\partial \omega / \partial H)(T)\), with similar absolute values, has been observed by us on \(\text{Fe}_{50}\text{Ni}_{x}\text{Mn}_{50-x}\) with \(x = 35\) and 36.5 at% Ni. These alloys definitely show RSG states for \(T \approx 50\ K\). We therefore conclude that the presence of mixed magnetic behavior or RSG phases inhibits a reliable determination of \(\partial \omega / \partial H\) at low temperatures.

For antiferromagnetic Invar alloys, which exhibit – as we have seen – substantial spontaneous volume magnetostriction (cf. fig. 23), only a tiny forced volume magnetostriction occurs. This is seen from our data of \(\omega(H)\) for AF \(\text{Fe}_{50.3}\text{Ni}_{26.5}\text{Mn}_{23.2}\) (\(T_N = 160\ K\)) in fig. 25. The volume change in field is \(10^2 - 10^3\) times smaller than in ferromagnetic Invar (cf. fig. 24), and the \(\omega(H)\)-curves are not linear either. In conclusion, we claim that the forced volume magnetostriction is not a good quantity to specify magnetovolume effects in Invar systems – at least from an experimental point of view.

The same statement holds for the high-field susceptibility. In Stoner- or Heisenberg-type models, which have – regardless of their validity – often been used to describe Invar properties, \(\partial \omega / \partial H\) is proportional to the slope of the magnetization curve in high fields (above technical saturation) \((\partial M / \partial H)_T =\)

![Fig. 25. Relative volume change at constant temperatures (\(\Delta \omega\)) as a function of applied field strength for antiferromagnetic \(\text{Fe}_{50.3}\text{Ni}_{26.5}\text{Mn}_{23.2}\) Invar (after Acet et al. 1988b).](image-url)
\( \chi_{HF} \), which is called the 'high-field susceptibility'. Unfortunately, like the \( \omega(H) \)-curves, the \( M(H) \)-curves at \( T = \text{const.} \) are not linear either, especially, if \( T_C \) is approached. The values of \( \chi_{HF} \) determined experimentally depend on the maximum field-strength available. This has been demonstrated, e.g., on Fe-36.4 at% Ni by Yamada and Du Trémolet De Lacheisserie (1984), who showed that the absolute values of \( \chi_{HF}(T) \) in \( H = 4 \text{T} \) in the \( 300 \leq T \leq 650 \text{K} \) range around \( T_C (\approx 537 \text{K}) \) are only half of the values taken in fields of \( H = 1 \text{T} \). At low temperatures in alloys with mixed magnetic phases, the problem of defining reliable \( \chi_{HF} \)-values is even more severe. In a spin glass (or RSG) the magnetization never reaches technical saturation, at least in fields of laboratory scale, and \( \chi_{HF} \) is therefore always ill-defined.

Consequently, like \( \partial \omega/\partial H \), the high-field susceptibility \( \chi_{HF} \) is also not a suitable quantity for comparison of experimental results on Invar with what theoretical model so ever [see, e.g., discrepancies in the paper by Kakehashi (1982), comparing experimental data of \( \chi_{HF} \) and \( \partial \omega/\partial H \) of FeNi with his results within the local-environment model].

4.4. Pressure dependence of Curie (Néel) temperatures and magnetization

From the large changes of the volume with magnetic field as well as concentration ('internal pressure'), one can expect large changes in the magnetic moment and the Curie or Néel temperatures with external pressure in Invar. This is known since a long time and experimentally well confirmed, at least for ferromagnetic Invar alloys. For not too high pressures (roughly up to 20 kbar), the Curie and Néel temperatures of Invar decrease linearly with pressure, so that values of \( dT_C/dp \) (K/kbar) can be defined. Figure 26 shows a plot of \( (dT_C/dp) \) or \( (dT_N/dp) \) versus electron concentration \( (e/a) \) as taken from the literature for FeNi (open dots) (Leger et al. 1972, Hausch 1973), disordered FePt (open triangles) and FePd (solid triangles downwards) (Honda Memorial Series 1978), Fe_{65}(NiMn)$_{35}$ (open squares) (Nakamura et al. 1971), NiMn (full dots) (Arnold and Kamarad 1980), NiCr (full triangles upright) (Tange et al. 1981), for an Elinvar-alloy Fe$_{52}$Ni$_{36}$Cr$_{12}$ (divided circle) (Hausch 1973), for antiferromagnetic Fe$_{70}$Mn$_{30}$ (cross) (Fujimori 1966) as well as for \( \gamma \)-Fe precipitations in Cu (plus sign) (Liu and Ingalls 1979). One salient feature of fig. 26 is the huge increase of \( -dT_C/dp \) in the ferromagnetic range from a positive value of \( dT_C/dp = +0.32 \text{K/kbar} \) for pure Ni to values of roughly \( -8 \text{K/kbar} \) for Fe$_{65}$Ni$_{27.2}$Mn$_{7.8}$. Less recognized by experimentalists (and in theory) as seen from the available amount of data, but to our feeling even more important, is the fact that in antiferromagnetic Invar appreciable values up to \( dT_N/dp = -2.5 \text{K/kbar} \) are reached too. Note that fig. 26 resembles very much the presentation of the spontaneous volume magnetostriction \( \omega_0(e/a) \) in fig. 23. A large volume magnetostriction occurs in the same \( e/a \)-ranges where large depressions of the Curie and Néel temperatures are observed. The large decrease of the ordering temperature with pressure is thus an important Invar characteristic feature, since it is present in both, FM and AF systems. Remember that plots like in fig. 26 or fig. 23 could be

\( (\chi_{HF})_T \), which is called the 'high-field susceptibility'. Unfortunately, like the \( \omega(H) \)-curves, the \( M(H) \)-curves at \( T = \text{const.} \) are not linear either, especially, if \( T_C \) is approached. The values of \( \chi_{HF} \) determined experimentally depend on the maximum field-strength available. This has been demonstrated, e.g., on Fe-36.4 at% Ni by Yamada and Du Trémolet De Lacheisserie (1984), who showed that the absolute values of \( \chi_{HF}(T) \) in \( H = 4 \text{T} \) in the \( 300 \leq T \leq 650 \text{K} \) range around \( T_C (\approx 537 \text{K}) \) are only half of the values taken in fields of \( H = 1 \text{T} \). At low temperatures in alloys with mixed magnetic phases, the problem of defining reliable \( \chi_{HF} \)-values is even more severe. In a spin glass (or RSG) the magnetization never reaches technical saturation, at least in fields of laboratory scale, and \( \chi_{HF} \) is therefore always ill-defined.

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4.4. Pressure dependence of Curie (Néel) temperatures and magnetization

From the large changes of the volume with magnetic field as well as concentration ('internal pressure'), one can expect large changes in the magnetic moment and the Curie or Néel temperatures with external pressure in Invar. This is known since a long time and experimentally well confirmed, at least for ferromagnetic Invar alloys. For not too high pressures (roughly up to 20 kbar), the Curie and Néel temperatures of Invar decrease linearly with pressure, so that values of \( dT_C/dp \) (K/kbar) can be defined. Figure 26 shows a plot of \( (dT_C/dp) \) or \( (dT_N/dp) \) versus electron concentration \( (e/a) \) as taken from the literature for FeNi (open dots) (Leger et al. 1972, Hausch 1973), disordered FePt (open triangles) and FePd (solid triangles downwards) (Honda Memorial Series 1978), Fe$_{65}$(NiMn)$_{35}$ (open squares) (Nakamura et al. 1971), NiMn (full dots) (Arnold and Kamarad 1980), NiCr (full triangles upright) (Tange et al. 1981), for an Elinvar-alloy Fe$_{52}$Ni$_{36}$Cr$_{12}$ (divided circle) (Hausch 1973), for antiferromagnetic Fe$_{70}$Mn$_{30}$ (cross) (Fujimori 1966) as well as for \( \gamma \)-Fe precipitations in Cu (plus sign) (Liu and Ingalls 1979). One salient feature of fig. 26 is the huge increase of \( -dT_C/dp \) in the ferromagnetic range from a positive value of \( dT_C/dp = +0.32 \text{K/kbar} \) for pure Ni to values of roughly \( -8 \text{K/kbar} \) for Fe$_{65}$Ni$_{27.2}$Mn$_{7.8}$. Less recognized by experimentalists (and in theory) as seen from the available amount of data, but to our feeling even more important, is the fact that in antiferromagnetic Invar appreciable values up to \( dT_N/dp = -2.5 \text{K/kbar} \) are reached too. Note that fig. 26 resembles very much the presentation of the spontaneous volume magnetostriction \( \omega_0(e/a) \) in fig. 23. A large volume magnetostriction occurs in the same \( e/a \)-ranges where large depressions of the Curie and Néel temperatures are observed. The large decrease of the ordering temperature with pressure is thus an important Invar characteristic feature, since it is present in both, FM and AF systems. Remember that plots like in fig. 26 or fig. 23 could be
obtained neither for the forced volume magnetostriction $\partial \omega / \partial H$ nor for the high-field susceptibility $\chi_{HF}$, because both quantities are negligibly small in antiferromagnetic Invar alloys. This supports the statement given at the end of the last chapter concerning the relevance of absolute values of $\partial \omega / \partial H$ and $\chi_{HF}$ for the understanding of the Invar effect.

As mentioned above, from the theoretical side commonly Stoner-type 'ansätze' have been used to explain ferromagnetic Invar behavior. For a homogeneous weak itinerant ferromagnetic (WIF) Wohlfarth (1983) claimed $-(d T_C / dp)$ to be proportional to $1 / T_C$. This is by no means correct for Invar as seen from fig. 27, where $-(d T_C / dp)$ versus the Curie and Néel temperatures are plotted [data from the same references as in fig. 26, for amorphous FeZr from Shirakawa et al. (1983)]. In all FM-Invar obviously $-(d T_C / dp)$ decreases linearly with increasing $T_C$, at least if the Curie temperatures are not too low. This was proposed to be valid for inhomogeneous ferromagnetic alloys by Wagner and Wohlfarth (1981). It is doubtful at present to what extend FePt alloys are 'inhomogeneous' ferromagnets. Moreover, a comprehensive theoretical description of Invar has to explain the contrasting fact that in antiferromagnetic Invar alloys obviously $-(d T_N / dp)$ increases linearly with $T_N$, as revealed in fig. 27.

If the Curie temperature is dependent on pressure, the magnetization of a FM Invar alloys should be pressure dependent as well. From the thermodynamic relation

$$ (\partial \omega / \partial H)_p = -(\partial M / \partial p)_H, \quad (4) $$

we can see that $\partial M / \partial p$, like $d T_C / dp$, is negative, since $\partial \omega / \partial H$ – irrespective
Fig. 27. Pressure dependence of the Curie temperatures $dT_C/dp$ for ferromagnetic and of Néel temperatures $dT_N/dp$ for antiferromagnetic Invar alloys versus $T_C$ and $T_N$, respectively (for references see text). Note the increase in $-dT_N/dp$ with $T_N$, in contrast to the decrease of $dT_C/dp$ with $T_C$ in the systems with FM order.

of its absolute value— is always positive. This is shown in fig. 28, where the pressure dependence of the spontaneous magnetization (relative to the magnetization at zero pressure) at 4.2 K and room temperature for Fe$_{65}$Ni$_{35}$ and disordered Fe$_{72}$Pt$_{28}$ is given (after Hayashi and Mori 1981). For Fe$_{65}$Ni$_{35}$ the magnetization decreases almost linearly with pressures up to about 20 kbar. The pressure coefficients, $(dM/dp)/M(0)$, are $-4.7 \times 10^{-3}$ kbar$^{-1}$ at 4.2 K and $-1.1 \times 10^{-2}$ kbar$^{-1}$ at RT, respectively. On the other hand, for Fe$_{72}$Pt$_{28}$ the pressure

Fig. 28. Relative pressure dependence of the magnetization $M(p)/M(0)$ versus pressure $p$ for FeNi Invar and FePt Invar (d = disordered) at 4.2 K and room temperature (after Hayashi and Mori 1981).
coefficient of the magnetization at 4.2 K \((dM/dp)/M(0) = -7 \times 10^{-4} \text{kbar}^{-1}\) is an order of magnitude smaller than in FeNi. At RT, for small pressures \((p < 3 \text{kbar})\), one finds the initial decreases of \((dM/dp)/M(0) = -2.4 \times 10^{-2} \text{kbar}^{-1}\) for Fe\(_{72}\)Pt\(_{28}\) to be of the same order of magnitude as in Fe\(_{65}\)Ni\(_{35}\), but at higher pressures a rapid, nonlinear decrease of the magnetization of Fe\(_{72}\)Pt\(_{28}\) is observed. This is due to the fact that the Curie temperature \((T_C = 380 \text{ K for } p = 0)\) decreases to about \(T_C = 310 \text{ K at } p = 20 \text{kbar}\), thus lies only slightly above RT.

Similar differences between the two systems have been observed in the pressure dependence of the spontaneous volume magnetostriction \(\omega_s(p)\) (Oomi and Mori 1981). These authors also have shown that Fe\(_{65}\)Ni\(_{26}\)Mn\(_9\) becomes magnetically 'soft' in the RSG range (Oomi and Mori 1983) so that part of the magnetic 'softness' of Fe\(_{65}\)Ni\(_{35}\) in comparison to the magnetic 'hardness' of Fe\(_{72}\)Pt\(_{28}\) at low temperatures is due to the presence of mixed magnetism in Fe\(_{65}\)Ni\(_{35}\). Nevertheless, the magnetic instability, which causes the Invar anomalies, obviously starts from zero temperature for FeNi, but it appears only at higher temperatures for FePt. This fact has intrigued people for a long time. We think that it is explainable within a modern band picture of Invar, as we will show below. Principally, there is no difference in the origin of the Invar effect in FeNi and FePt and thus all Invar systems.

4.5. Magnetic properties

4.5.1. Concentration dependence of Curie and Néel temperatures

Figure 29 shows Curie and Néel temperatures versus electron per atom ratio for different binary and ternary Invar systems in fcc \(\gamma\)-structure. Data are mainly due to Richter and Pepperhoff (1976). Open circles give the respective ordering temperatures of the pure elements. Figure 29 reveals some further systematics in the magnetism of 3d-elements and alloys and consequently the Invar effect. Comparison to figs. 22 and 23 shows that in the ranges \(e/a = 8.5-8.7\) for the FM systems and \(e/a = 7.5-7.7\) for the AF systems, where minimum thermal expansion (fig. 22) and maximum volume magnetostriction (fig. 23) occur, the Curie and Néel temperatures steeply decrease. In the range \(e/a = 8.1-8.3\), where \(\alpha_{RT}\) reaches a maximum. (cf., fig. 22) and the spontaneous volume magnetostriction vanishes (cf., fig. 23), the ordering temperatures in fig. 29 approach small values. As we have seen above, this is the \(e/a\)-range, where SG and RSG phases are observed. One might call these alloys 'itinerant spin glasses' since they differ appreciably from the common dilute spin glasses usually understood in a local-moment picture. Itinerant SG models have been proposed by Kakehashi (1988a) on the basis of the nonlinearity of the couplings between local moments, and by Wasserman (1989b) on the basis of the results of the 'fixed spin moment' method (see section 6).

In this context, it is important to note that binary and ternary alloys composed of Fe with 3d-elements on the right-hand side of Fe in the periodic table (e.g., FeNi, FeCo, FeNiCo) do not show the itinerant spin-glass state, but undergo a structural phase transition prior of reaching the SG phase. In contrast to that, all
Fig. 29. Curie and Néel temperatures as a function of the electron concentration for different fcc transition element alloys (after Richter and Pepperhoff 1976). Note that in comparison to figs. 22 and 23 in the FM (and AF) Invar range the transition temperatures decrease with falling (rising) electron concentration. SG phases occur around \( e/a = 8.3 \), where the transition temperatures reach minimum values.

Binary and ternary alloy systems containing at least one 3d-element that is positioned left of Fe in the periodic table (e.g., CoMn, CoV, FeNiMn, FeNiCr), do show the itinerant SG phase. As will be demonstrated later (section 6) this difference can be understood on a theoretical basis. If the moment–volume instabilities (Invar effect) become overwhelming, the systems undergo a structural phase transition before reaching the itinerant SG phase. If the lattice is continuously enlarged by alloying elements with larger atomic volume (i.e., those 3d-elements left of Fe in the periodic table), the systems can reach the SG state and the antiferromagnetic \( e/a \) range as well. Here they show AF Invar behavior, since – as to be seen later – e.g., fcc Mn shows moment–volume instabilities too.

4.5.2. Concentration dependence of magnetic moment

For a long time it was thought that the deviation of the average magnetic moment \( \bar{\mu} \) from the Slater–Pauling curve, like it is observed in FeNi alloys on approach to the \( \gamma - \alpha \)-transition (see fig. 5) is one of the most prominent features of Invar, since it gives obvious indication for the instability of the magnetic moment. On the other hand, as seen in fig. 6 for FePt and fig. 7 for FePd, there are alloy systems which show the Invar effect on approach to the \( \gamma - \alpha \) instability limit, their Curie temperatures decrease in the respective concentration range, but the moment does not deviate from the Slater–Pauling curve. Consequently, deviation of the average magnetic moment from the Slater–Pauling curve is not an Invar relevant feature.
With respect to the discussion given in the preceding chapter, this can also be understood in the modern band picture. If the lattice volume is enlarged by alloying Fe with Pt and Pd, which both have a larger atomic volume than Fe, the internal pressure in the systems is reduced and there is ‘room’ for large moments and large volumes of the Fe atoms. No deviation of the moment from the Salter–Pauling curve is the consequence. If the Pt or Pd concentration is reduced, the internal pressure rises, and at a certain limit the moment–volume instabilities become too large for the lattice to ‘bear’. A $\gamma-\alpha$ transition is then the consequence.

These features have been described in a finite-temperature model by Kakehashi (1985) (see also below, section 6.2). Decisive in this model is the amplitude of the local moment as defined in a spin-fluctuation picture (Kakehashi 1985). This amplitude might be experimentally accessible through neutron diffraction, but the amount of this type of data for Invar is scarce, and also their interpretation is problematic (see Kakehashi 1985).

4.5.3. Temperature dependence of the magnetization
Another characteristic property of Invar alloys is their unusual temperature dependence of the magnetization (or of the magnetic moment) in comparison to ‘ordinary’ ferromagnets. For the latter we assume, for simplicity, Brillouin behavior to be valid. To show the principal differences, we again choose the two Invar compositions Fe$_{65}$Ni$_{35}$ and disordered and ordered Fe$_{72}$Pt$_{28}$. In fig. 30, following data of Yamada et al. (1982), the reduced spontaneous magnetization $M_s(T, H = 0)/M_s(T = 0, H = 0) = M_s(T, 0)/M_s(0, 0)$ versus the reduced tempera-

![Fig. 30. Relative spontaneous magnetization $M_s(T, 0)/M_s(0, 0)$ versus relative temperature $T/T_c$ for ordered and disordered Fe$_{72}$Pt$_{28}$ and Fe$_{65}$Ni$_{35}$ Invar alloys. The full curve gives the behavior for pure Ni (Brillouin function) [all data after Yamada et al. (1982)]. The inset shows the low-temperature behavior on an enlarged scale.](image-url)
ture $T/T_C$ is plotted. The inset shows in enlarged scale the low-temperature behavior. Note that initially, with rising $T$ the magnetization in all three Invar alloys decreases faster than in Ni. This means that assuming a Bloch dependence of the form,

$$M_s(T, 0) = M_s(0, 0) \left[ 1 - 2.61 \frac{g \mu_B}{M_s(0, 0)} \left( \frac{k_B T}{4 \pi D_m} \right)^{3/2} \right],$$  

the spin wave stiffness $D_m$ in Invar alloys, as determined from the temperature dependence of the magnetization, is smaller than in, e.g., Ni, expressing the magnetic softness of the alloys (see section 4.7 below). However, if one analyzes the available low-temperature magnetization data of Invar more closely, a $T^{3/2}$ dependence of $M_s(T)$ can never be fitted in a sizeable range. Attempts to fit Stoner expressions with $M_s(T, 0)/M_s(0, 0) \propto 1 - a T^2$ also failed. Best fits resulted from a combination of two dependences in the form (Maruyama 1986),

$$M_s(T, 0) = M_s(0, 0) \left[ 1 - a T^{3/2} - b T^n \right],$$  

with $n = 2 \pm 0.3$ and $a, b = \text{const}$. The validity of this equation is footed on the assumption that in Invar alloys, besides spin-wave excitations (which are definitely present as we will see below, section 4.6), a second type of excitation occurs. Since the physical nature of the second excitation is not fully understood at present, eq. (6) is more or less a working hypothesis. We shall show, however, in section 6 that on the basis of modern theories of Invar its presence can be made at least qualitatively plausible.

One should also note that a determination of reliable values of $M_s(0, 0)$ is problematic, since as discussed in section 4.3, the $M(H)$ curves in Invar often do not saturate [XHF values depend on the maximum field available, see, e.g., Ono and Chikazumi (1974)], leading to errors in the extrapolation of the $M(H)$-curves to $H = 0$. Secondly, if pure ferromagnetic ground states do not exist because of the occurrence of SG-phases or for metallurgical reasons [e.g., Fe$_{65}$Ni$_{35}$ contains some antiferromagnetic precipitations (Zähres et al. 1988) and ordered Fe$_{72}$Pt$_{28}$ shows some premartensitic transformation at roughly $M_{ps} = 60$ K (Maruyama et al. 1986)], neither $M_s(0, 0)$ nor the low-temperature dependence of $M_s(T)$ – regardless of what type of fit is attempted – can be determined satisfactorily.

In turning back to fig. 30 we can see that with increasing temperature the magnetization of Fe$_{65}$Ni$_{35}$ always stays below the Ni- or Brillouin curve, whereas disordered and ordered Fe$_{72}$Pt$_{28}$ both cross the Brillouin curve at some temperatures, and on approach to $T_C$ show a higher magnetization than a respective ordinary FM. This explains – starting from the ‘crossing’ temperatures – the experimentally observed sharp decrease of the spontaneous volume magnetostriction (and consequently negative values in the $\alpha(T)$ curves) on both Fe$_{72}$Pt$_{28}$ alloys (Sumiyama et al. 1976). Simultaneously, the sharp drop of $M_s(T)$ on approach to $T_C$ is accompanied by a steep rise in $\alpha(T)$ to positive values for $T > T_C$. As one can see in fig. 30, for $T > T_C$ the magnetization in all Invar alloys has a long ‘tail’
up to $T/T_C = 1.2$ or higher. This reflects the presence of moment-volume instabilities for $T > T_C$ in Invar, as we have already seen above, when discussing other physical properties. In other words, the splitting does not vanish at $T_C$, when we interpret these features in a band picture. The 'tail' in $M_s(T)$ also makes a correct determination of the Curie temperatures from $M_s(T)$ curves almost impossible. This does not improve very much, when Arrot plots from magnetization measurements $M(H, T)$ are used. The $M^2$ versus $H/M$ curves for temperatures around $T_C$ are not linear (Shen et al. 1985).

4.6. Spin waves and spin-wave stiffness

As mentioned in the preceding section, spin waves are exited with increasing temperature in Invar alloys. Figure 31 shows the spin-wave dispersion in the three major directions of the Brillouin zone as measured by inelastic neutron-scattering (INS) at 11 K for ordered Fe$_{72}$Pt$_{28}$ (Ishikawa et al. 1980) and for Fe$_{65}$Ni$_{35}$ at

![Spin-wave dispersion](image_url)
4.2 K (Kohgi et al. 1976). For Fe$_3$Pt at low $q$-vectors a quadratic dispersion relation of the form $E = D_{sw}q^2$ holds, with a spin-wave stiffness $D_{sw} = 80 \pm 5$ meV $\text{Å}^2$, independent of the lattice direction. For Fe$_{65}$Ni$_{35}$, $D_{sw} = 142 \pm 5$ meV $\text{Å}^2$ is found. There are negligibly small energy gaps of the order of 0.05 meV at $q = 0$ in both systems.

On approach to the zone boundary $q = \pi/a$ in Fe$_3$Pt, only in the $[\zeta 00]$ direction a negative magnon dispersion with a limiting value of $E_{BZ} [\zeta 00] \approx 40$ meV is found. There is some uncertainty in the data (see dots and squares in fig. 31) because phonon peaks cross through the spin-wave maxima near the $[\zeta 00]$ zone boundary (Ishikawa et al. 1980). In both systems, however, the quadratic behavior of $E(q)$ continues for both directions $[\zeta \zeta 0]$ and $[\zeta \zeta \zeta]$ up to energies above 80 meV, and no saturation of the magnon energies could be detected. Stoner-type excitations are not found either, in spite of intensive search at $q = \pi/a$ (and lower $q$). The magnon peaks in the INS spectra just become very broad at high energies as expressed by the error bars in fig. 31. The Stoner boundary in both systems thus should be located above 80 meV. Since Invar properties start to appear at very low temperatures, Stoner excitations cannot be, if they exist at all, the origin of the Invar effect.

In most of the publications of neutron scattering on Invar alloys it is quoted that the spin-wave stiffness renormalizes with temperature (provided $E = D_{sw}q^2$ holds) according to,

$$D_{sw}(T) = D_{sw}(0)[1 - A(T/T_c)^{5/2}] .$$

This equation is based on the Heisenberg model (magnon–magnon damping), thus $A$ is proportional to the exchange interaction (see Fernandez-Baca et al. 1987). As shown in fig. 32a, eq. (7) seems to be valid almost up to $T_c$ in ordered Fe$_{72}$Pt$_{28}$ (Ishikawa et al. 1979) and amorphous Fe$_{86}$B$_{14}$ (open triangles; Fernandez-Baca et al. 1987, closed triangles; Ishikawa et al. 1981), while it holds well for Fe$_{65}$Ni$_{35}$ up to $(T/T_c) = 0.7$ (Ishikawa et al. 1979) but not at higher temperatures, and is also not valid for Fe$_2$(Zr$_{0.7}$Nb$_{0.3}$) at high temperatures [see crosses in fig. 32 (after Onodera et al. 1982)]. Surprisingly, eq. (7) is valid for Fe$_{50}$Ni$_{50}$, only for $T/T_c > 0.6$.

Since Invar systems are definitely not pure Heisenberg-like, the validity of eq. (7) to describe the temperature dependence of the spin-wave stiffness (equivalent to the renormalization of the spin-wave energy) with temperature is doubtful anyhow. Moreover, the experimental data are not sufficient in number and accuracy so that – as revealed in fig. 32b – a plot of $D_{sw}$ versus $(T/T_c)^2$ describes the results as well as, and at high temperatures close to $T_c$ even better than the $(T/T_c)^{5/2}$ dependence. However, note that both plots in figs. 32a,b are not very conclusive for $(T/T_c) < 0.4$, because of the ‘compression’ of the low-temperature range. Since Invar systems are neither purely Heisenberg nor purely Stoner-like, one can again use the working hypothesis that in Invar two different excitations – magnons and ‘Invar-type’ spin fluctuations – are present simultaneously. A phenomenological approach (Izuyama and Kubo 1964) to the theory of magnetic
Fig. 32. (a) Spin wave stiffness constant $D_{sw}$ versus $(T/T_c)^{5/2}$ for Fe$_{50}$Ni$_{50}$, Fe$_{65}$Ni$_{35}$ and ordered Fe$_{72}$Pt$_{28}$ (all data after Ishikawa et al. (1979)), as well as amorphous Fe$_{66}$B$_{14}$ [open triangles: Fernandez-Baca et al. (1987), closed triangles: Ishikawa et al. (1981)] and the Laves phase compound Fe$_2$(Zr$_{0.7}$Nb$_{0.3}$) (after Onodera et al. 1982). (b) Same data as in (a) plotted versus $(T/T_c)^2$.

materials with collective (itinerant) electrons, leads to the following temperature dependence of the magnon spectrum,

$$\omega(q, T) = \omega(q, 0)(1 - AT^2 - BT^{5/2})$$

where the $T^2$ term is determined by Fermi excitations of the electrons and the $T^{5/2}$ term by spin fluctuations. Theoretical approaches for evaluating the coefficients $A$ and $B$ have been discussed recently by Silin and Solontzov (1985, 1987). They showed that the anomalous frequency and temperature dependence of the magnon-spectrum rigidity is caused by the influence of the dynamics of the crystal lattice on the spin fluctuations in itinerant ferromagnets. Applied to Invar, their results could lead to an understanding of a well-known intriguing problem of Invar, i.e., the difference in spin-wave stiffness $D_{sw}$ as determined from neutron scattering, and $D_m$ as determined from the temperature dependence of the magnetization according to eq. (5), i.e., from a $T^{3/2}$ law.
In table 6 we list some values of $D_{sw}$ and $D_m$ as they have been taken from different references. Ratios of $D_{sw}/D_m = 1.3-2.5$ are observed in Invar, while in non-Invar systems the ratio is always equal to unity. Note that in Fe$_{50}$Ni$_{50}$, although this compound shows a small invar effect ($\omega_{40} = 0.5 \times 10^{-2}$), $D_{sw}/D_m$ is also unity. The discrepancies between $D_{sw}$ and $D_m$ have led Ishikawa et al. (1986a) to the statement that in Invar some ‘hidden excitations’ exist which are not sensed by neutrons, i.e., on a short time scale. However, they do contribute to the magnetization, which means they are ‘seen’ in a long time-scale experiment. Although the problem is not yet fully solved at present, we think (see section 6) that the volume coupled high-spin–low-spin-state transitions, clearly revealed in modern band calculations, could give rise to these ‘hidden excitations’. However, since band calculations are so far only done for $T = 0$, the dynamics and nature of the high-spin–low-spin-state transition and the temperature dependence involved remains an open question at present.

Without going into the details of the dynamics we remark here that Ishikawa et al. (1979) and Onodera et al. (1981) have proposed that the rapid demagnetization of Invar-alloys with temperature is a consequence of an anomalous spin-wave damping. Indeed, in a neutron-scattering experiment longitudinal spin fluctuations (like possibly the high-spin–low-spin-state transition) could cause a considerable increase in the linewidth $\Gamma_q$. INS experiments on crystalline Fe$_3$Pt and Fe$_{65}$Ni$_{35}$ (Ishikawa et al. 1979, Onodera et al. 1981) and amorphous Fe$_{86}$B$_{14}$ (Ishikawa et al. 1981) revealed that the spin-wave linewidths are not proportional.

### Table 6

<table>
<thead>
<tr>
<th>Invar systems</th>
<th>$T_c$ (K)</th>
<th>$D_{sw}$ (meV Å$^2$)</th>
<th>$D_m$ (meV Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{65}$Ni$</em>{35}$</td>
<td>503</td>
<td>142 ± 5 [1]</td>
<td>59 [1]</td>
</tr>
<tr>
<td>Fe$<em>{50}$Ni$</em>{50}$</td>
<td>785</td>
<td>220 ± 10 [2]</td>
<td>225 [2]</td>
</tr>
<tr>
<td>o. Fe$<em>{72}$Pt$</em>{28}$</td>
<td>504</td>
<td>80 ± 5 [2]</td>
<td>60 [2]</td>
</tr>
<tr>
<td>Fe$<em>3$(Zr$</em>{0.7}$Nb$_{0.3}$)</td>
<td>380</td>
<td>350 ± 50 [3]</td>
<td>125 ± 10 [3]</td>
</tr>
<tr>
<td>a-Fe$<em>{86}$B$</em>{14}$</td>
<td>556</td>
<td>125 ± 7 [4]</td>
<td>65 [5]</td>
</tr>
<tr>
<td>a-Fe$<em>{82}$B$</em>{18}$</td>
<td>617</td>
<td>165 [4]</td>
<td>71 [5]</td>
</tr>
<tr>
<td>a-Fe$<em>{75}$Si$</em>{15}$B$_{10}$</td>
<td>710</td>
<td>220 ± 10 [6]</td>
<td>127 ± 5 [7]</td>
</tr>
<tr>
<td>a-Fe$<em>{70}$Ni$</em>{20}$Zr$_{10}$</td>
<td>455</td>
<td>112 [8]</td>
<td>72 [9]</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Non-Invar systems</th>
<th>$T_c$ (K)</th>
<th>$D_{sw}$ (meV Å$^2$)</th>
<th>$D_m$ (meV Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Fe$<em>{65}$Ni$</em>{35}$)$<em>{72}$P$</em>{18}$B$_6$Al$_3$</td>
<td>114 ± 10 [10]</td>
<td>115 ± 3 [10]</td>
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<tr>
<td>Fe</td>
<td>310 ± 10</td>
<td>285 ± 10</td>
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<tr>
<td>Ni</td>
<td>420</td>
<td>415</td>
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References:
to $q^4$ like in ordinary ferromagnets, but rather follow the empirical relation

$$\Gamma_q \propto \Gamma_0 (1 + CT^\alpha)q^2,$$

with $\alpha = 1$ for Fe$_3$Pt and $\alpha \leq 1$ for Fe$_{65}$Ni$_{35}$. Although there are some contradictions in the literature [e.g., Fernandez-Baca et al. (1987) report $\Gamma_q \propto q^4 [T \ln(k_B T/E_q)]^2$ for a-Fe$_{86}$B$_{14}$ in the range 445–520 K $< T_c = 556$ K], and the analysis depends on the spectral weight functions chosen and on resolution limits, there is no doubt that for Invar alloys the linewidths $\Gamma_q$ are much larger than for ordinary Heisenberg or Stoner-type ferromagnets. This is seen from fig. 33 where we have collected all data $\Gamma_q(q)$ known to us for Fe$_3$Pt and Fe$_{65}$Ni$_{35}$ from the literature. For $T < T_c$ (data from Ishikawa et al. 1979, 1986b) $\Gamma_q$ roughly follows the $q^2$-dependence in both alloys (and Fe$_{50}$Ni$_{50}$ as well). Although there is some ambiguity in the exact value of the exponent, a dependence $\Gamma_q \propto q^4$ like in Pd$_2$MnSn or EuO is definitely not observed in Invar.

![Fig. 33. Double logarithmic plot of the spin-wave linewidth $\Gamma(q, T = \text{const.})$ versus wave vector $q$ at constant temperatures for ordered Fe$_3$Pt and Fe$_{65}$Ni$_{35}$. Some data for Fe$_{50}$Ni$_{50}$ and the Heisenberg ferromagnets Pd$_2$MnSn and EuO are also shown for comparison [all data after Ishikawa et al. (1979, 1986b)].](image-url)
The insufficient accuracy of the data in fig. 33 also does not allow a closer examination of the critical behavior. At $T \approx T_C$ (about 4 K above) in Fe$_3$Pt one observes $\Gamma_q \propto q^n$ with $n = 2.7 \pm 0.1$, which is larger than $n = 2.48$, as expected from critical-scaling theory and observed in pure $\alpha$-Fe (Mezei 1982). For $T > T_C$ at all $q$-values investigated, there is a further nonmonotonic increase in linewidth above the values found at $T_C$ in Fe$_3$Pt (Bóni et al. 1986) and Fe$_{65}$Ni$_{35}$ (Tajima et al. 1987). This might be considered an Invar-typical feature, since a fit to the data using a spin-fluctuation dependence of the form $\Gamma_q \propto q/(q^2 + \kappa^2)$, where $\kappa$ is an inverse correlation length, did not give satisfying results either. More accurate measurements are obviously necessary to achieve a conclusive answer concerning the nature of the dynamical behavior in Invar alloys. Doubtlessly, however, the polarization of the 3d-bands persists to far above $T_C$, as already shown by Collins (1965) by means of paramagnetic neutron-scattering on Fe$_{65}$Ni$_{35}$. At twice the Curie temperature, he found an iron moment of $(1.4 \pm 0.4)\mu_B$.

4.7. Elastic properties

As mentioned in the introduction, Guillaume found already in 1920 that the temperature coefficient of the elastic modulus of FeNi becomes very small around 45 at% Ni (Elinvar effect). Since then the elastic properties of FeNi and other Elinvar systems (see section 2) have been studied extensively, mainly because of their technical importance. Good summaries on the elastic properties of polycrystalline Invar and Elinvar alloys—expressed by the bulk, shear and elastic moduli as functions of alloy composition, temperature, and magnetic field—have been given in the Honda Memorial Series on the Physics and Application of Invar Alloys (1978) (chs. 7, 23 and 24). Of more fundamental importance for the physical understanding of Invar, are studies of the elastic behavior of single-crystalline material, i.e., the determination of elastic constants. A cubic single crystal has three independent elastic constants $c_{11}$, $c_{12}$ and $c_{44}$. There are also three different modes $i$ of propagation for a sound wave with velocities $v_i$. These velocities are related to the elastic constants ($\rho = $ density) as indicated in table 7. One can see that a measurement of sound velocities in the [110] direction on one

### Table 7

<table>
<thead>
<tr>
<th>Direction of propagation</th>
<th>Mode $i$</th>
<th>Direction of polarization</th>
<th>$\rho v_i^2 = c_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100]</td>
<td>L</td>
<td>–</td>
<td>$c_{11}$</td>
</tr>
<tr>
<td>[100]</td>
<td>T</td>
<td>indifferent</td>
<td>$c_{44}$</td>
</tr>
<tr>
<td>[110]</td>
<td>L</td>
<td>[110]</td>
<td>$\frac{1}{2}(c_{11} + c_{12} + 2c_{44}) \equiv C_L$</td>
</tr>
<tr>
<td>[110]</td>
<td>T$_1$</td>
<td>[110]</td>
<td>$\frac{1}{2}(c_{11} - c_{12}) \equiv C'$</td>
</tr>
<tr>
<td>[110]</td>
<td>T$_2$</td>
<td>[001]</td>
<td>$c_{44} \equiv C_{44}$</td>
</tr>
<tr>
<td>[111]</td>
<td>L</td>
<td>–</td>
<td>$\frac{1}{2}(c_{11} + 2c_{12} + 3c_{44})$</td>
</tr>
<tr>
<td>[111]</td>
<td>T</td>
<td>indifferent</td>
<td>$\frac{1}{2}(c_{11} - c_{12} + c_{44})$</td>
</tr>
</tbody>
</table>
sample allows to determine the three independent constants $c_{11}$, $c_{12}$, $c_{44}$. Commonly one expresses the elastic properties of crystals with cubic symmetry through three elastic constants $C_L$, $C'$ and $C_{44}$ (‘Capital C’) which are defined by linear combinations of the $c_{ij}$ (see table 7) and related directly to the modes of propagation in the [110] direction by,

$$
C_L = \rho v_L^2, \quad C' = \rho v_{T_1}^2, \quad C_{44} = \rho v_{T_2}^2.
$$

The bulk modulus is given by

$$
B = C_L - \frac{1}{3} C' - C_{44} = \frac{1}{3} (c_{11} + 2c_{12}).
$$

$C_L$ expresses a compression mode accompanied by a change in volume, $C'$ corresponds to a pure shear mode with an expansion along one of the [110] axis (tetragonal distortion). $C_{44}$ corresponds to a pure shear mode with an expansion occurring along the [111] axis (trigonal distortion). Both shear modes leave the volume unchanged.

For ferromagnetic Invar alloys, a large softening in the shear behavior occurs when the temperature is lowered below the respective Curie temperatures. This is seen in figs. 34 and 35. In fig. 34 the elastic constant $C'$ is plotted versus

![Graph showing elastic shear constant C' as a function of temperature](image)

Fig. 34. Elastic shear constant $C'$ as a function of temperature, as determined in ultrasonic measurements for pure Ni, Fe$_{55}$Ni$_{35}$ and Fe$_{59}$Ni$_{41}$ by Renaud (1988) and ordered and disordered Fe$_{72}$Pt$_{28}$ by Hausch (1974). Data from inelastic neutron-scattering (INS) as determined by Endoh et al. (1977) for Fe$_{65}$Ni$_{35}$ and by Tajima et al. (1976) for ordered Fe$_{72}$Pt$_{28}$ are also given. The respective Curie temperatures are marked by arrows.
temperature. Data for pure Ni and FeNi alloys are taken from a recent thesis by Renaud (1988), who measured the elastic constants in zero magnetic field in the temperature range from 77 to 1500 K by an ultrasonic method. The data for Fe$_{72}$Pt$_{28}$ (disordered and ordered) originate from the work of Hausch (1974), who measured $C'(T)$ in zero field and a field of 0.6 T to suppress domain reorientation effects ($\Delta E$ effect). There is, however, no difference in the principal behavior of $C'(T)$, although the $\Delta E$ effect in $C'$ is large at low temperatures (in FePt $\approx$ 30% for $T \to 0$) but small at $T_C$. Figure 34 also shows the results of $C'(T)$ from fits to phonon dispersion curves as measured on Fe$_{65}$Ni$_{35}$ with inelastic neutron scattering (INS) by Endoh et al. (1977) and by Tajima et al. (1976) on ordered Fe$_{72}$Pt$_{28}$. Note that there is roughly equivalence between the neutron data and the ultrasonic measurements at low temperatures, while for $T$ around $T_C$ or $T > T_C$ the sound velocities from INS measurements are somewhat higher than the velocities from ultrasonic (US) measurements. This discrepancy might be due to the difference between so-called ‘zero’ sound (neutrons) and first sound (ultrasonics) (Endoh et al. 1977).

Grosso modo, the temperature behavior of the shear mode $C'(T)$ is, however, similar in the INS and US investigations. Both methods show that substantial softening is present in the Invar systems on lowering the temperature, setting in almost at the respective Curie temperatures (see arrows in fig. 34). Note also that the softening is absent in Ni, where for $T < T_C$ even a small increase in slope of $C'(T)$ with respect to the range $T > T_C$ is observed. Without going into details, we mention here that the softening in the shear constant $C' = \frac{1}{2}(c_{11} - c_{12})$ was explained in a band picture within the Stoner model for Fe$_3$Pt by Pettifor and Roy (1978).

As can be seen from fig. 35, the shear constant $C_{44}$ as a function of temperature shows almost the same overall behavior as $C'(T)$. The data in fig. 35 are taken from the same references as the data in fig. 34. Note that in Fe$_{65}$Ni$_{35}$ below about 50 K there is a sudden increase in $C_{44}$ on lowering the temperature, which also occurs in the shear constant $C'$ as seen in fig. 34 (Hausch 1976). This increase is absent in Fe$_3$Pt (Hausch 1974) and obviously related to the magnetic inhomogeneities present in Fe$_{65}$Ni$_{35}$ at low $T$ (see magnetic phase diagram in fig. 5). This is supported by the observation of the low-temperature behavior of $C_L(T)$ on Fe$_{65}$Ni$_{30.5}$Mn$_{4.5}$ (Shiga et al. 1988) (cf., fig. 36) where below the SG-freezing temperature $T_f$ a sudden increase in $C_L$, i.e., a lattice hardening, sets in.

This leads us to the discussion of the temperature behavior of the longitudinal elastic constant $C_L(T)$, which is shown in fig. 36. Data for Ni and FeNi alloys (in zero field) are due to Renaud (1988), for Fe$_{72}$Pt$_{28}$ (ordered and disordered in $B = 0.6$ T) again to Hausch (1974) and for FeNiMn to Shiga et al. (1988). The INS results for Fe$_{72}$Pt$_{28}$ are calculated from data by Tajima et al. (1976), the results for Fe$_{65}$Ni$_{35}$ are due to Endoh (1979). In comparison to the shear behavior $C'(T)$ and $C_{44}(T)$, the temperature dependence of the elastic compression $C_L(T)$ of Invar shows the following different features:

1. In the US measurements again a substantial lattice softening is observed, which, however, sets in at temperatures far above $T_C$. 
Fig. 35. Elastic shear constant $C_{44}$ as a function of temperature, as determined in ultrasonic measurements, for pure Ni, Fe$_{65}$Ni$_{35}$ and Fe$_{59}$Ni$_{41}$ by Renaud (1988) and ordered and disordered Fe$_{72}$Pt$_{28}$ by Hausch (1974). Data from inelastic neutron-scattering (INS) for ordered Fe$_{72}$Pt$_{28}$ by Tajima et al. (1976) are also given. The respective Curie temperatures are marked by arrows.

Fig. 36. Longitudinal elastic constant $C_L$ versus temperature, as determined in ultrasonic measurements, for pure Ni, Fe$_{65}$Ni$_{35}$, Fe$_{59}$Ni$_{41}$ and Fe$_{50}$Ni$_{50}$ by Renaud (1988), for ordered and disordered Fe$_{72}$Pt$_{28}$ by Hausch (1974) and for Fe$_{59}$Ni$_{30}$Mn$_{40}$ by Shiga et al. (1988). Data from inelastic neutron scattering (INS) for ordered Fe$_{72}$Pt$_{28}$ by Tajima et al. (1976) and Fe$_{65}$Ni$_{35}$ by Endoh (1979) are also given. The arrows mark the respective Curie temperatures.
(2) $C_1(T)$ has a minimum below $T_C$, therefore irrespective of the increase through the spin-glass freezing (see FeNiMn and Fe$_{63}$Ni$_{35}$ in fig. 36), there is
(3) increasing lattice stiffness for $T \rightarrow 0$.
(4) In inelastic neutron scattering, i.e., in zero sound, the softening in the longitudinal mode is not observed, neither in FeNi nor in FePt (cf. INS data in fig. 36).

The latter observation (4) is reminiscent of the situation described in the preceding section, where we discussed the differences in spin-wave stiffness observed on short time scales with neutrons and long time scales in magnetization. Obviously, the Invar-typical volume changing high-spin–low-spin-state transitions (see section 6) are also not sensed in the phonon dispersion curves $\omega(q, T)$ determined by neutron spectroscopy on short time scales (zero sound). Remember that this is different when the – volume conserving – transversal (shear) modes are investigated. The elastic constants $C'(T)$ and $C_{44}(T)$ as derived from the phonon-dispersion curves $\omega(q, T)$ in the [110] direction for $q < 0.4 \text{ Å}^{-1}$ in INS are almost equivalent (cf. figs. 34 and 35) to those determined from the transversal sound velocity $v_T(T)$ in the US experiments at much smaller $q$-values (smaller frequencies).

In this context we mention that an unexpected ‘central peak’ around $\omega = 0$ was observed in Fe$_3$Pt in addition to the soft-phonon side peaks (Tajima et al. 1976) in the [110] direction in the INS spectra, the intensity of this peak developing gradually on lowering of the temperature from 100 to 4.2 K. Tajima et al. (1976) suggested that the central peak was of static origin, possibly related to the premartensitic transformation in Fe$_3$Pt, but a detailed explanation for its physical origin was never given. It remains an open question whether central peak is indeed only of static origin.

In total, the frequency and temperature dependence of the longitudinal modes in Invar are not yet fully understood. It is necessary to investigate further these dependences, i.e., the dynamical and temperature behavior of the electron-phonon coupling in the presence of longitudinal and/or transverse spin fluctuations. Since – as we have seen – phonon softening occurs only at small wave vectors $q$, i.e., at long wavelength, only distant forces are changed and the softening is not dominated by near-neighbour forces. This means that band-type calculations provide the right approach for the understanding of the problem. For this it is helpful to know absolute values of the purely magnetic contributions to the different modes. The determination is possible in a reliable way on the basis of the high-temperature ultrasonic investigations by Renaud (1988). Extrapolating the high-temperature ($T \gg T_C$) linear behavior of $C_1(T)$, $C'(T)$ and $C_{44}(T)$ to $T = 0$ provides the respective paramagnetic references for the temperature range $T < T_C$. The magnetic contributions to the elastic constants are then given by the difference between the paramagnetic reference and the actually measured data (cf. figs. 34–36). Assuming similar linear dependences to hold for $T \gg T_C$ in Fe$_{72}$Pt$_{28}$, the magnetic contributions to the elastic constants (at ultrasonic frequencies) can be evaluated for these alloys (with larger error) too. Note again the difficulty discussed above that the reference is paramagnetic and not ‘nonmagnetic’ as would be actually required.
By means of eq. (11) the magnetic contribution to the bulk modulus $\Delta B_m(T)$ can then also be determined. The result is shown in fig. 37, where $\Delta B_m$ versus the reduced temperature $T/T_C$ is plotted. The inset shows in the same type of plot the shear behavior $\Delta C'_m(T/T_C)$. $\Delta C_{44m}(T/T_C)$ (not shown in the figure) has almost the same quantitative features as $\Delta C'_m(T/T_C)$. Note the onset of the softening in $\Delta B_m$, the longitudinal (volume changing) compression at $T > T_C$, where the pure shear modes $\Delta C'_m$ (and $\Delta C_{44m}$) are zero, and the large drop in $\Delta B_m$ in the range just below $T_C$, where the softening in shear is also of minor influence. $\Delta B_m(T/T_C)$ has for all Invar alloys a characteristic minimum, which is largest in disordered Fe$_{72}$Pt$_{28}$, still observable in Fe$_{50}$Ni$_{50}$ and not present in pure Ni, for which $\Delta B_m(T/T_C) = 0$ in the whole temperature range investigated (points omitted for clearness in fig. 37). A further characteristic feature is the increasing lattice hardness (rise in $\Delta B_m$) on approach to zero temperature, which is more or less present in all Invar alloys in fig. 37. The differences between Fe$_{65}$Ni$_{35}$ and Fe$_{72}$Pt$_{28}$ are probably due to the differences in the forced volume magnetostriction $\partial \sigma / \partial H$, which is large in Fe$_{65}$Ni$_{35}$ at low temperatures but small in Fe$_{72}$Pt$_{28}$. Finally, we infer from fig. 37 that in the $0 \leq T/T_C \leq 0.3$ range the magnetic contributions due to shear deformation $\Delta C'_m$, $\Delta C_{44m}$ are larger or of the same order of magnitude (Fe$_{65}$Ni$_{35}$) as the magnetic contribution to the bulk modulus. Although many efforts (see, e.g., Hausch 1979) have been done to understand the salient features of the elastic behavior of Invar as presented in fig. 37, no

Fig. 37. Magnetic contribution to the bulk modulus $\Delta B_m$ versus reduced temperature $T/T_C$ as calculated by use of eq. (11) from the ultrasonic data in figs. 34–36 by extrapolating the results in the paramagnetic high-temperature range to $T = 0$ K, and taking the difference between extrapolated and measured values. Note the characteristic softening on approach to $T_C$, as well as its persistence to far above $T_C$. The inset shows the magnetic contribution to the shear constant $\Delta C'_m$ versus $T/T_C$ determined in the same fashion for 3 alloys (symbols as in large scale figure). Note that the shear softening sets in at $T_C$ and increases continuously on lowering the temperature.
satisfying answer has been given so far. Especially, the model of weak itinerant ferromagnetism due to Wohlfarth (1976) is not applicable at all.

The situation is complicated by the fact that antiferromagnetic Invar alloys, in spite of having a substantial spontaneous volume magnetostriction (cf. fig. 23) exhibit a completely different temperature (and frequency) dependence of their elastic constants in comparison to ferromagnetic Invar. This is shown in fig. 38, where the temperature dependences of $C_L$ (fig. 38a), $C'$ (fig. 38b) and $C_{44}$ (fig. 38c) are given. Ultra sound measurements on a single crystal of Fe$_{60}$Mn$_{40}$ (open triangles) are due to Renaud (1988), on a crystal with the almost the same composition Fe$_{61.5}$Mn$_{38.5}$ (solid dots) from Lenkkeri (1981) and for Mn$_{85}$Ni$_{15}$ (full curve) and Mn$_{81.5}$Ni$_{18.5}$ (dashed curve) from Hausch et al. (1983). The INS results

![Graph of Elastic Constants](image)

Fig. 38. Elastic constants $C_L$, $C'$ and $C_{44}$ as a function of temperature for single-crystalline antiferromagnetic Invar alloys. Ultra-sound results on Fe$_{60}$Mn$_{40}$ (open triangles) are due to Renaud (1988), on a crystal with almost the same composition Fe$_{61.5}$Mn$_{38.5}$ (solid dots) to Lenkkeri (1981), on Mn$_{85}$Ni$_{15}$ (full curves) and Mn$_{81.5}$Ni$_{18.5}$ (dashed curves) to Hausch et al. (1983). The INS results on Fe$_{60}$Mn$_{40}$ have been determined by Endoh et al. (1981). Note that in contrast to ferromagnetic Invar (figs. 34–37), softening in antiferromagnetic Invar is noticeable only in $C'(T)$ right at the respective Néel temperatures (arrows).
on Fe\textsubscript{70}Mn\textsubscript{30} (solid triangles) have been determined by Endoh et al. (1981). We infer from fig. 38 that:

1. the softening in the longitudinal mode \(C_L(T)\) is absent in AF Invar alloys, there is just a small dip at \(T = T_N\);
2. the discrepancy in the \(C_L(T)\) behavior between short-time neutron investigations (INS) and US measurements at lower frequencies does not exist, both methods show lattice hardening in the range \(T < T_N\);
3. Under trigonal distortion in \(C_{44}(T)\), almost no softening effect is observable;
4. the only relaxation occurs in the tetragonal shear distortion in \(C'(T)\) right at \(T_N\), where a sudden – first-order like – drop takes place at temperatures just below the respective Néel temperatures, while on further lowering of \(T\) there is again a linear increase in \(C'(T)\), with a slope similar to the one in the paramagnetic range. A determination of the magnetic contribution to the bulk modulus \(\Delta B_m(T)\) [eq. (11)] consequently gives a sudden hardening for AF Invar at \(T = T_N\). For \(T < T_N\), \(\Delta B_m(T)\) is positive and almost constant to \(T = 0\).

If we assume – for good reasons, as demonstrated above – that the Invar effect in FM and AF systems is of the same physical origin, the results presented in fig. 38 are puzzling, and up to now not understood. In our opinion, the elastic behavior is strongly influenced by the atomistic type of magnetic ordering, which is quite different in the FM and AF systems. The FM single-crystalline systems presented above all have a collinear spin structure, while both AF systems in fig. 38 have a noncollinear spin structure. It is known from neutron-scattering experiments on FeMn (Endoh and Ishikawa 1971) and MnNi (Kawarazaki et al. 1988) that the spins in both alloys point in the [111] direction of the unit cell. This could lead to a ‘compensation effect’ between the spin components in different lattice directions under compression and trigonal shear (\(C_L\) and \(C_{44}\)) and explain the absence of softening in these modes. Moreover, the first-order like transition observed in \(C'(T)\) right at \(T_N\) in the AF crystals can also be made plausible. It is known (Endoh and Ishikawa 1971) that fct FeMn has a collinear spin structure. Thus, under tetragonal distortion there is possibly a sudden transition from a non collinear to a collinear spin arrangement for \(T \leq T_N\).

4.8. Specific heat

Since for the understanding of the Invar effect (and magnetoelastic properties in general) electronic and phonic contributions are of equal importance, measurements of the specific heat provide an important tool to study both contributions simultaneously.

We first turn to an analysis of the electronic contribution, i.e., of the \(\gamma\)-term in the electronic specific heat. Since in Invar alloys the instability of the moment is accompanied by a drastic change in density of states (DOS) of the d-electrons near the Fermi surface (see section 6), unusually high \(\gamma\)-terms have been thought for a long time to be an Invar-typical feature. In fig. 39 we have plotted \(\gamma\)-values as derived from the low-temperature specific heat as a function of \(e/a\) for
Fig. 39. $\gamma$-coefficients of the low-temperature electronic specific-heat as a function of the electron concentration for different Invar and non-Invar transition metal alloys (for references see text). Note that the enhanced values observed in the range $e/a = 8.2-8.6$ are caused by superposition of two linear terms in the specific heat at low temperatures, the electronic $\gamma$-term and a spin-glass or re-entrant spin-glass (RSG) term originating from the low-energy excitations in the disordered state. For other details see text.

Several features are immediately obvious from fig. 39. First, it seems that in the FM Invar range for $e/a > 8.5$, where the spontaneous volume magnetostriction $\omega_{\delta 0}$ is large (cf. fig. 23), the $\gamma$-values increase to twice or three times the values observed in pure Ni or non-Invar systems like NiV or NiMn. Note, however, that, secondly, in ordered and disordered FePt ($\gamma = 9.6 \text{ mJ/mol K}^2$ and $\gamma = 7.6 \text{ mJ/mol K}^2$, respectively) ‘normal’ $\gamma$-values like in Ni have been measured. Third, in the range $e/a = 8.3-8.5$, where $\omega_{\delta 0}$ vanishes, the $\gamma$ values become very large, up to $30 \text{ mJ/mol K}^2$. This increase in $\gamma$ has nothing to do with the Invar effect. It originates from magnetic low-energy excitations in the SG or RSG phases, which are present in the respective alloys at low temperatures. It is well-known that spin glasses exhibit a linear magnetic specific heat as a function of temperature up to temperatures above the respective freezing temperatures, so
that the total specific heat in the alloy systems in question is given by,

\[ C_p(T) = \gamma T + \alpha_{\text{SG}} T + \beta T^3. \]

(12)

In plots of \((C_p/T)\) versus \(T^2\), from which the electronic \(\gamma\) terms (and the Debye-like \(\beta\) lattice term) are usually derived, both linear \(T\) terms are superimposed and cannot be distinguished. To separate the two terms, we recently have carefully reinvestigated the low-temperature magnetic properties [AC susceptibility \(\chi'(T)\) and \(\chi''(T)\)] and the specific heat in zero external field and in magnetic fields up to 6 T of FM RSG alloys \(\text{Fe}_{57}\text{Ni}_{23}\text{Cr}_{20}\) with \(T_c = 23\) K, \(T_I = 19\) K (Lecomte and Schubert 1988) and \(\text{Fe}_{50}\text{Ni}_{35}\text{Mn}_{15}\) with \(T_c = 208\) K, \(T_I = 60\) K (Lecomte et al. 1988a), as well as an AF alloy \(\text{Fe}_{50}\text{Ni}_{28}\text{Mn}_{22}\) (Lecomte et al. 1988b) with \(T_N = 80\) K, which is, however, not a good long-range ordered AF. Our \(\gamma\) values as derived from the zero-field measurements are marked by an ‘L’ in fig. 39. They are in agreement with the earlier data. Yet, in FM + RSG samples SG-typical maxima are observed in the magnetic specific heat above the respective \(T_I\). If one tries to ‘freeze out’ the SG contributions by measurement of \(C_p(T)\) in a magnetic field, appreciable reductions in the magnetic specific heat are observed. The \(\gamma\)-values as determined in \(H = 6\) T are marked by an additional ‘H’ in fig. 39. Yet, these values do not represent the ‘true’ \(\gamma\)-values of the alloys, since the relative reduction \(C_p(H)/C_p(0)\) at constant \(T\) (e.g., 4.2 K) shows a linear decrease with increasing \(H\) up to 6 T, and is therefore far from saturation.

The previous discussion shows that an enhanced \(\gamma\)-term of the electronic specific heat is not an Invar-typical feature. The magnitude of \(\gamma\) is apparently not directly correlated to the magnetoelastic properties (compare figs. 23 and 39). There is no maximum in \(\gamma(e/a)\) in fig. 39 in the AF-range, where \(\omega_{s0}\) (fig. 23) reaches peak values too. The only alloy investigated there, i.e., \(\text{Fe}_{67}\text{Mn}_{11}\text{C}_{12}\) [see cross with question mark in fig. 39; data from Gupta et al. (1964)], is very likely inhomogeneous (mixture of \(\epsilon\)-martensite and \(\gamma\)-phase), and for a comprehensive discussion not reliable. The same holds for the carbon-stabilized sample \(\text{Fe}_{65}\text{Ni}_{28}\text{C}_{7}\) [see circle with question mark in fig. 39 (Gupta et al. 1964)]. Also \(\text{Fe}_{65}\text{Ni}_{35}\) (\(e/a = 8.7\)) exhibits mixed magnetic behavior at low temperatures (cf. magnetic phase diagram in fig. 5). In conclusion, reliable \(\gamma\)-values for Invar are of the order of \(10–11\) mJ/mol K\(^2\) and thus they are not ‘anomalous’ with respect to Ni or other magnetic non-Invar systems. We have indicated the range where \(\gamma\) is enhanced through SG contributions by the dashed-dotted line in fig. 39.

Concerning the lattice contribution to the specific heat, doubtlessly the softening of the lattice observed in Invar in the elastic properties should be directly reflected in the respective Debye temperatures \(\theta_D\). In fig. 40 we have plotted the Debye temperature versus \(e/a\) as collected from the literature. Data symbols and references are identical to the references in fig. 39. Although most of the Debye temperatures in fig. 40 have been determined from the low-temperature specific heat and thus are \(\theta_D(T = 0) = \theta_D^0\), the analogy of the concentration dependence of \(\theta_D^0(e/a)\) to the spontaneous volume magnetostriction \(\omega_s(e/a)\) (see fig. 23) is obvious. Low \(\theta_D^0\), i.e., lattice softening, occurs in the FM range around \(e/
Fig. 40. Debye temperatures $\theta_D$ versus electron concentration $e/a$ for different Invar and non-Invar transition element alloys (for references see text). Note the 'softening' in the ferromagnetic Invar range around $e/a = 8.7$. With some uncertainty softening also occurs in the antiferromagnetic Invar range around $e/a = 7.7$.

Not many specific-heat measurements have been reported in the literature for an intermediate temperature range between about 20 K and room temperature. Measurements of $C_p(T)$ in this range, however, provide important informations about Invar. First, recent studies on Fe$_{50}$Ni$_{35}$Mn$_{15}$ (Lecomte et al. 1988b) and Fe$_{57}$Ni$_{23}$Cr$_{20}$ (Lecomte and Schubert 1988) reveal that Debye-like fits to the lattice contribution of the specific heat in the temperature range from 20 to 120 K lead to an appreciable reduction in the Debye temperature. $\theta_D$ is – as expected – a function of temperature, $\theta_D(T)$. Around 50 K, $\theta_D$ drops from the low-temperature values $\theta_D^0$ to values $\theta_D$ at higher $T$ and remains constant up to 120 K. The drop can be as large as 50 to 60 K, as shown by the data indicated by ‘L’ and ‘∞’ in fig. 40. In principle, the behavior of $\theta_D(T)$ can also be derived from the phonon-frequency distribution in inelastic neutron scattering and the temperature dependence of the elastic constants. Again, few data are available here. We mention the result on Fe$_{72}$Pt$_{28}$, where Hausch (1974) derived $\theta_D^0 = 320$ K for the ordered alloy from the elastic constants (see value indicated by ‘H’ in fig. 40), while the specific-heat measurements by Sumiyama et al. (1976) gave $\theta_D^0 = 525 \pm 20$ K for the ordered alloy (see triangle with question mark in fig. 40) and $\theta_D^0 = 450 \pm 10$ K for the disordered alloy, respectively. The same group, on the other hand, reported $\theta_D^0 = 460$ K for ordered Fe$_5$Pt earlier (see Kawarazaki et al. 1972). On
approach to $T_c$ all elastic constants increase with increasing temperature, as has been demonstrated in the preceding section. This lattice hardening should manifest itself in an increase in the Debye temperature and $\theta_D(T)$ should thus show a minimum. Yet, to our knowledge, no data are available so far to support this expectation.

A second extraordinary feature found in the $C_p(T)$ dependence of certain Invar alloys at elevated temperatures is the absence of the peak or 'smeared out' behavior at the respective Curie or Néel temperatures. This is seen in fig. 41.

![Fig. 41. Total specific heat as a function of temperature $C_p(T)$ as measured on Fe$_{56}$Ni$_x$Mn$_{44-x}$ alloys with different Ni concentrations in the 0–300 K range by Derayabin et al. (1983) and in the high-temperature range by Bendick et al. (1978). Because of mismatch in absolute values and differences in concentrations, the right-hand scale, valid for the high-temperature data, is shifted downwards by 4 J/mol K with respect to the left-hand scale, valid for the low-temperature data. The crossover range is indicated by the vertical dashed-dotted line. Note the absence of any ordering peaks at $T_c$, $T_N$, if these ordering temperatures are small ($\approx 300$ K) and the smeared out behavior if $T_c$, $T_N$ lies within the broad 'bump' in the 350–500 K range. All these features are caused by volume fluctuations associated with the moment instabilities. Remarkable are also the fluctuations in $C_p(T)$ occurring in the paramagnetic high-temperature range. The inset shows the magnetic phase diagram (Acet et al. 1988a). Arrows mark the concentrations for which $C_p(T)$ curves are given.](image-url)
where the total specific heat $C_p$ versus $T$ is plotted for alloys of the system $\text{Fe}_{50}\text{Ni}_{35}\text{Mn}_{15}$. Data in the 0–300 K range have been reported by Deryabin et al. (1983), the high-temperature data by Bendick et al. (1978). Unpublished data on two alloys with $x = 10$ and 40 at% Ni by Pepperhoff are also added. Unfortunately, there is a mismatch between the absolute values in $C_p$ of the two groups, even when the Ni concentration is equal. We have indicated this by the vertical dashed-dotted line. The specific-heat values of Deryabin et al. (1983) are about 4 J/mol K too small at RT, as we have recently confirmed (see fig. 42), but coincide with our data up to about 150 K. Nevertheless, we see from fig. 41 that there is almost no anomaly in $C_p(T)$ accompanying the onset of magnetic long-range order, if the ordering temperatures lie in the range below RT. We have confirmed this on several alloys in the $\text{Fe}_{50}(\text{NiMn})_{50}$ system by using a quasi-adiabatic heat-pulse technique (Schubert et al. 1989), in which the samples ($\approx$7 g) are in thermal equilibrium at each measuring temperature. Deryabin et al. (1983) also find no anomaly at $T_C$, $T_N$ in $\text{Fe}_{65}\text{Ni}_{35-x}\text{Cr}_x$ with $x = 6$ ($T_C = 270$ K), $x = 10$ ($T_C = 160$ K) and $x = 20$ (SRO AF + FM alloy, $T_N = 100$ K) at% Cr.

If the Curie (Néel) temperatures increase to 400–500 K, maxima in $C_p(T)$ accompanying the ordering are present, as can be seen in fig. 41 for the two alloys with $x = 10$ at% Ni ($T_N = 385$ K) and $x = 40$ at% Ni ($T_C = 475$ K). Yet, both samples are far from showing any type of critical behavior at $T_N$, i.e., a $\lambda$-type anomaly as one would expect. Note also that the high-temperature specific-heat

\[ C_p(T) = 3' T + \beta T^3 \]

with $3' = 4$ mJ/mol K$^2$ and $\theta_D = 360$ K. The crosses show the temperature dependence of the thermal expansion coefficient $\alpha(T)$ (after Bendick et al. 1977) (right-hand scale). The dashed curve is a calculated Grüneisen curve with $\theta_D = 360$ K.
data in fig. 3 show the same behavior for Fe$_{65}$Ni$_{35}$. Only if $T_C$ lies beyond the respective temperature (energy) range, as, e.g., in Fe$_{60}$Ni$_{40}$ ($T_C = 600$ K) and Fe$_{50}$Ni$_{50}$ ($T_C = 785$ K), sharp peaks in $C_p(T)$ appear at the transition temperatures. Note that for all Invar alloys in fig. 41 and fig. 3 large excess specific heat is found in the paramagnetic range, with broad maxima between 400 and 500 K. We are certain that all these contributions are of magnetic origin and manifest the presence of the instability of the moments (spin fluctuations) for $T \gg T_C$, $T_N$, since they are also observed in ordered Fe$_{72}$Pt$_{28}$ (see Wassermann 1989a) and AF Fe$_{100-x}$Mn$_x$ with $x = 31.7, 39.7$ and $50.2$ at% Mn (see Stamm 1988).

The moment instabilities are accompanied by lattice instabilities, as it is shown in fig. 42, where $C_p(T)$ and $\alpha(T)$ for Fe$_{50}$Ni$_{30}$Mn$_{10}$ as measured in the range from zero to 1200 K are plotted. Data for $C_p(T)$ from 0 K to RT have been determined by Schubert et al. (1989) and from RT to 1200 K by Bendick et al. (1978). The full curve is calculated from $C_p(T) = \gamma T + \beta T^3$, with $\gamma = 4$ mJ/mol k$^2$ and $\theta_D = 360$ K. Note again the absence of a peak in $C_p(T)$ at the ordering temperature, and the excess specific heat in the paramagnetic range for $T > T_C$ with a broad maximum around 500 K. The thermal expansion $\alpha(T)$ [data are a combination of results from Acet et al. (1988a) and Bendick et al. (1977)] simultaneously has no anomaly at $T = T_C$, but also shows a broad ‘bump’ around 500 K and lies above the Grüneisen curve (dashed line in fig. 42), which has been calculated with $\theta_D = 360$ K and fitted to the experimental results in the low-temperature range.

We can summarize the results of this section in the following way:

1. Extraordinary high $\gamma$-values determined from the specific heat in Invar alloys at low temperatures are not Invar typical, but result from contributions of mixed magnetic phases (SG, RSG or similar). ‘True’ $\gamma$ values of Invar (FM and AF) are of the order of 10–11 mJ/mol K$^2$, thus not much higher than in, e.g., pure Ni ($\gamma = 7$ mJ/mol K$^2$).

2. A plot of the Debye temperatures determined at low (or elevated) temperatures versus the electron per atom ratio $(e/a)$ shows analogy to the spontaneous volume magnetostriction of the lattice accompanying the Invar effect.

3. Ferromagnetic and antiferromagnetic Invar alloys with $100 \text{ K} \leq T_C, T_N \leq 400 \text{ K}$, show no anomaly in the specific heat $C_p(T)$ at the respective ordering temperatures.

4. Large excess specific-heat contributions are, however, observed in $C_p(T)$ in all AF and FM systems, even in ordered Fe$_{72}$Pt$_{28}$, in the range around 500 K. If the Curie (or Néel) temperatures reach values above this temperature range, the bump in the specific heat at about 500 K is still present, and a second $\lambda$-type anomaly occurs at the respective $T_C$ (or $T_N$). If the Curie (Néel) temperatures lie in the range around 500 K, both anomalies overlap and lead to a ‘smeared out’ maximum of $C_p(T)$ in the range around the ordering temperature.

5. The anomalies in the specific heat are accompanied by anomalies in the volume of the alloys. This fact reveals the principal, Invar-typical property because it means that the magnetic instabilities or moment fluctuations are coupled to lattice instabilities or phonon fluctuations.

Invar is thus a problem which calls for the theoretical understanding not only of
the nature of the ground state but – more important to our feeling – also of the finite-temperature effects involved.

5. Survey of theories on Invar

5.1. Early Invar models

In order to understand the Invar effect in 3d-transition metal alloys, there have been two different basic approaches. One is based on the localized electron picture (Heisenberg model), in which each atom has its own permanent and temperature independent moment. The other is based on the itinerant picture of magnetism (Stoner model) giving rise to the understanding of the composition dependence of the average moment (Slater–Pauling curve), with the drawback that the band splitting vanishes at $T_C$, which is, as we have seen, not the case in Invar. Within the years more than 20 different models for the understanding of the Invar effect have been published. The most important ones are listed in table 8. The early local models stressed the metallurgical and/or magnetic inhomogeneity as Invar relevant, since in the archetypical Invar system FeNi the magnetovolume effects reach a maximum near the $\gamma$–$\alpha$ transition at Fe$_{65}$Ni$_{35}$, where simultaneously a strong deviation of the average magnetic moment (or magnetization) from the Slater–Pauling curve was observed. This group includes the ‘model of latent antiferromagnetism’ (Kondorsky and Sedov 1960, Jo 1976), the ‘local models with different short-range order’ (Sidorov and Doroshenko 1966, Dubinin et al. 1971) the ‘local environment models’ (Schlosser 1971, Kanamori 1974), the ‘inhomogeneity models’ (Kachi and Asano 1969, Shimizu 1979) as well as a ‘Zener-type model’ (Colling and Carr 1970). With the detection of the Invar effect on ordered Fe$_3$Pt, a system which neither shows mixed magnetic behavior nor deviation of the average moment from the Slater–Pauling curve, all these models came principally into doubt.

Important within the group of local models is the historically widely debated phenomenological ‘2$\gamma$-state model’ of Weiss (1963). Already in 1963 Weiss claimed that $\gamma$-Fe can exist in two different magnetic states, the AF low-spin (LS) state $\gamma_1$, which has a small magnetic moment ($\mu = 0.5\mu_B$) and small volume ($a = 3.57 \text{ Å}$), and the FM high-spin (HS) state $\gamma_2$, with large moment ($\mu = 2.87\mu_B$) and large volume ($a = 3.64 \text{ Å}$). For FeNi alloys, Weiss assumed the energy difference between the two states to be a function of the Ni concentration, so that in Fe$_{65}$Ni$_{35}$ the $\gamma_2$-state is the ground state, and with rising temperature the increasing population of the low-volume $\gamma_1$-state leads to the compensation of the lattice expansion. The Weiss model was extended and refined (Bendick et al. 1979, Chikazumi 1980) but a direct proof of its validity was never given. We shall see later that within modern band calculations, i.e., in a completely different type of approach, the 2$\gamma$-state model will experience a certain revival.

Therefore, instead of stressing the inhomogeneity, homogeneous models on the basis of an itinerant picture seemed more promising. Mathon and Wohlfarth (1968) and Wohlfarth (1969) considered Fe$_{65}$Ni$_{35}$ to be a weak itinerant fer-
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<th><strong>Local moment models</strong></th>
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<th><strong>Band models (cont’d)</strong></th>
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romagnet (WIF) and successfully explained many Invar properties on the basis of a Stoner-type band model. However, ordered Fe$_3$Pt is not a weak but a strong itinerant ferromagnet and the finding of Invar properties on this alloy thus puts the WIF approach also into doubt. Improvements of the itinerant model with distance-dependent band width proposed by Shiga and Nakamura (1969), and a CPA-type of approach by Hasegawa and Kanamori (1971) explained some of the Invar properties of FeNi and FePt, but failed to explain the finite temperature properties, especially in the paramagnetic range. Antiferromagnetic Invar was not discussed at all within all the models mentioned, and therefore, we can regard them all as ‘historical’.

5.2. Moment–volume instabilities in 3d-elements

In the late 1970s band calculations within the local spin density approximation (LSDA) predicted the existence of two ferromagnetic states for fcc Fe, a high-spin state with large moment and large volume and a low-spin state with low moment and volume. The main literature is summarized in 8.1 of table 8. Other methods (8.2–8.4 in table 8) gave similar results too. In fig. 43 we show a plot of the magnetic moment $\mu_{\text{Fe}}$ versus the radius of the Wigner–Seitz cell $r_{\text{ws}}$ for fcc Fe as taken from different references. Note that all theoretical methods applied reveal more or less the instability of the Fe-moment and the coexistence of a HS, LS and

![Fig. 43. Magnetic moment of fcc Fe as a function of the radius of the Wigner–Seitz cell $r_{\text{ws}}$ as calculated by Bagayoko and Callaway (1983) (dashed-dotted lines), Wang et al. (1985) (dashed lines), Moruzzi et al. (1986) (full lines for the stability ranges in zero field), Krasko (1987) (plus signs and dashed-double dotted lines) and within a disordered local-moment (DLM) picture by Pinski et al. (1986) (crosses). The arrow marks the lattice constant as determined for AF coherent $\gamma$-Fe precipitations in Cu (Bendick et al. 1977).](image-url)
a non-magnetic (NM) state within an instability range of $2.640 \leq r_{ws} \leq 2.704$ a.u. or $3.570 \AA \leq a \leq 3.657$ Å of the lattice constant, respectively. This range coincides with the instability range in the phenomenological model of Weiss (1963), which thus experiences retrospectively a certain confirmation. This is better seen in fig. 44a, where the total energy (relative to a minimum energy) as determined by Moruzzi et al. (1986) is plotted versus the Fe moment with $r_{ws}$ as a parameter. The HS, LS and NM states, characterized by energy minima in the curves for $r_{ws} = \text{const.}$, can clearly be distinguished, and thus remind of the Weiss picture.

Figure 44b shows $E - E_{\text{min}}$ as a function of $r_{ws}$ as determined by Moruzzi et al. (1986) (full curves) and by Krasko (1987) (dashed curves). Note that both methods of calculation result in almost the same overall behavior, but differ in absolute values. While Moruzzi et al. (1986) give an energy difference of about 15 mRy between the HS and the NM state, Krasko (1987) finds $\Delta E = 7.5$ mRy.

The moment–volume instability is by no means bound to fcc Fe, but occurs in other fcc elements as well. This is seen from fig. 45, where the magnetic moment $\mu$ versus $r_{ws}$ is plotted for fcc Fe and Co (Moruzzi et al. 1986) and fcc Mn (Brener et al. 1988). Note the instability in Co, which shows a transition from a FM HS state to a NM state, and Mn, where a transition from a ferromagnetic HS state to an antiferromagnetic ground state is observed. In this context it is most important to note that a computed moment of zero – like in the ground state of Mn – indicates only that the ground state is not ferromagnetic. The calculations cannot determine whether the ground state is non-magnetic or antiferromagnetic. For fcc

Fig. 44. (a) Total energy (relative to a minimum energy) versus magnetic moment for fcc Fe at different radii of the Wigner–Seitz cell $r_{ws}$ within the instability region (cf. fig. 43). Note the occurrence of high-moment or high-spin (HS) and low-moment or low-spin (LS) states, as characterized by minima in the curves (after Moruzzi et al. 1986), (NM) marks the non-magnetic states. (b) Total energy (relative to a minimum energy) versus radius of the Wigner–Seitz cell $r_{ws}$ as calculated by Moruzzi et al. (1986) (full curves) and Krasko (1987) (dashed curves) for fcc Fe.
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3.4 3.6 3.8 \( a (\text{Å}) \)

\[ \mu (\mu_B) \]

\( \text{Co} \)
\( \text{Fe} \)
\( \text{Mn} \)

\( \text{Mn} \)
\( \text{Fe(MM)} \)
\( \alpha\text{Fe} \)
\( \text{Co(FM)} \)

Fig. 45. Magnetic moment \( \mu \) (in \( \mu_B \)) versus radius of the Wigner-Seitz cell \( r_{ws} \) (in atomic units) for fcc Fe (full line), fcc Co (dashed-dotted line) [both after Moruzzi et al. (1986)], and for fcc Mn (after Brener et al. 1988). The dashed-dotted line shows the result for homogeneous pure amorphous Fe (Krompiewski et al. 1988).

Fig. 46. Normal-emission, spin-resolved energy-distribution curves for an epitaxially grown 11 Å thick fcc Fe film on a single-crystalline Cu₃Au substrate, using \( h\nu = 60 \text{ eV} \), s-polarized radiation (Carbone et al. 1988).
Mn it has been shown by additional wave-vector dependent susceptibility calculations (Fry et al. 1988) that the ground state has AF order. With respect to the occurrence of the Invar effect in amorphous alloys (a-FeB, a-FeZr) we show in fig. 45 that Krompiewski et al. (1988) have found an instability of the Fe-moment in amorphous, homogeneously magnetized a-FeB (dashed line).

An experimental proof that fcc Fe at large lattice constants is in the ferromagnetic HS state has been given by us (Carbone et al. 1988) recently through measurements of the spin-resolved energy distribution curves (SREDs) of a 11 Å γ-Fe film grown epitaxially on a Cu₃Au (001) single-crystalline substrate with \( a = 3.75 \) Å. Figure 46 shows the SREDs for this film, for which a high spin polarization (\( \geq 50\% \)) was also observed. The peak positions in the SREDs in fig. 46 are in good agreement with the calculated critical-point energies at \( \Gamma \) and X points in the Brillouin zone of fcc Fe at \( a = 7.0 \text{ a.u.} = 3.70 \) Å (Bagayoko and Callaway 1983). The shoulder in the majority-spin EDC at \( E_F \) can be attributed to \( X_{st} \), which is predicted to be at 0.2 eV binding energy. Since \( X_{st} \) determines the top of the majority spin d-bands, we conclude that fcc Fe is a strong FM for a lattice constant of 3.75 Å. This is in excellent agreement with the theoretical results (cf. fig. 43) and earlier magnetization measurements (Gradmann and

![Fig. 47. Magnetic moment \( m \) versus radius of the Wigner-Seitz \( r_{ws} \) for different 3d-elements in bcc lattice structure (after Moruzzi and Marcus 1988). The crosses mark the results for bcc Mn as calculated by Fry et al. (1987). Note the instabilities for bcc Mn, V and Cr. The arrows mark the respective equilibrium values of the lattice constants.](image-url)
Isbert 1980) for Fe on Cu$_x$Au$_{1-x}$, where a decrease in the Fe moment with increasing Cu concentration (decreasing lattice constant) was observed. On the other hand, the situation for fcc Fe when grown epitaxially on Cu(001) with $a = 3.61 \text{ Å}$ is still experimentally contradictory [see discussion in the paper by Carbone et al. (1988)]. FM and NM behavior has been observed, probably because at $a = 3.61 \text{ Å} = r_{ws} = 2.669$ a.u. one is right within the instability range of pure fcc Fe. On the other hand, coherent $\gamma$-Fe precipitations in Cu are definitely antiferromagnetic (Tsunoda et al. 1987, Macedo and Keune 1988) with $T_N = 67$ K at $a = 3.570 \text{ Å}$, but with a complicated canted spin structure of the Fe moments modulated in space (Tsunoda et al. 1988).

Finally, we show in fig. 47 that for 3d-elements in bcc lattice structure moment instabilities occur too. These results stem from very recent calculations by Moruzzi and Marcus (1988), who investigated carefully the complete 3d-series in bcc form. In fig. 47 we see that bcc Cr (full line) makes a HS–NM transition; bcc V (dashed-dotted line) and bcc Mn (dashed line and crosses from Fry et al. 1987) clearly make HS–LS–NM transitions around $r_{ws} = 3.5$ and $r_{ws} = 2.58$, respectively, while the curves for $\alpha$-Fe and bcc Co are continuous, which means that the moments of these elements are not unstable with respect to changes in the lattice constant.

6. Towards a new understanding of the Invar-effect

6.1. Theoretical evidence for high-spin–low-spin-state transitions in Invar alloys

Figure 48a shows constant energy contours projected into the moment–volume (or $r_{ws}$) plane as calculated for ordered Fe$_3$Ni with the FSM method by Moruzzi (1988). Figure 48b shows an analogous presentation (Entel and Schröter 1989) calculated with parameters determined from band-structure calculations using a Ginzburg–Landau like energy functional (Entel et al. 1989) for ordered Fe$_3$Pt. The zero-field solutions ($H = dE/dM = 0$) are given by the full curves labeled $H = 0$, the zero-pressure solutions ($p = -dE/dV = 0$) are given by the dashed lines labeled $p = 0$ in both diagrams, respectively. Note that these zero-pressure and zero-field equilibrium curves in both systems cross twice, at a HS state marked by ‘0’ and a LS state marked by ‘X’. In Fe$_3$Ni the HS state occurs at $r_{ws} = 2.6$ a.u. = 3.517 Å with $m = 1.5 \mu_B$/atom, the LS state at $r_{ws} = 2.55$ a.u. = 3.449 Å with $m = 0.47 \mu_B$/atom. The values for Fe$_3$Pt are $r_{ws} = 2.695$ a.u. = 3.645 Å with $m = 1.75 \mu_B$/atom for the HS state and $r_{ws} = 2.65$ a.u. = 3.584 Å with $m = 0.95 \mu_B$/atom for the LS state. We remark that the LS state in Fe$_3$Pt in fig. 48 might not be stable, but the absolute values gained in these calculations should not be overestimated anyhow. Important is the principally analogous behavior for both systems which is evident from fig. 48. Both systems show HS and LS states, reminiscent of the Weiss 2$\gamma$-states model (Weiss 1963).

This is also revealed in fig. 49, where the volume dependence of the total energy along the zero-field lines is given (Moruzzi 1988, Entel and Schröter 1989). For Fe$_3$Ni also the site-decomposed zero-field moments for Fe and Ni are
Fig. 48. Total-energy contours projected into the moment–volume (or \( r_{ws} \)) plane for (a) ordered \( \text{Fe}_3\text{Ni} \) calculated by Moruzzi (1988), and (b) ordered \( \text{Fe}_3\text{Pt} \) calculated by Entel and Schräter (1989) with the FSM method. The zero-field solutions \( H = \frac{dE}{dM} = 0 \) are given by the full curve labeled \( H = 0 \), the zero-pressure solutions \( p = -\frac{dE}{dV} = 0 \) by the dashed curve labeled \( p = 0 \) in both diagrams, respectively. Note that in both systems the zero-field and zero-pressure curves cross twice, corresponding to two energetically-stable states: a high-spin state (marked by '0') with large moment and large volume, and a low-spin state (marked by 'X') with small moment and small volume. The results are reminiscent of the phenomenological 2 \( \gamma \)-states model of Weiss (1963).

shown. In particular, the low energy-difference of the order of 1 mRy between the HS and LS states in both systems is obvious. Although the present results are valid at \( T = 0 \) only, one can imagine that the smallness of the energy barrier allows the LS state to be accessible with temperature (or pressure), since 1 mRy corresponds to roughly 150 K (or about 10 kbar considering the volume difference between HS and LS states).

From a band-theoretical point of view, thermal expansion is a direct consequence of the anharmonicity of the binding curves like in fig. 49. In non-Invar systems or pure 3d-metals usually the curves are skewed towards high volumes, reflecting positive anharmonicity and thus implying a tendency of the system to expand with increasing temperature (Moruzzi et al. 1988). In both Invar systems in fig. 49, on the other hand, the LS branch at low volumes effectively introduces a negative anharmonicity, which implies a tendency of the systems to contract with increasing temperature, which is indeed experimentally observed.
Moreover, we note a difference between Fe$_3$Ni and Fe$_3$Pt insofar as Fe$_3$Ni exhibits a saddle point at $r_{ws} = 2.55$ a.u., while in Fe$_3$Pt a real energy barrier is found with a height of about 1 mRy. The minima themselves show only an energy difference of about 0.3 mRy. Although again, for finite temperatures, the results in figs. 48 and 49 should not be taken too literally, this difference in the total energy curves makes some of the observed differences in the low-temperature behavior of these two Invar-systems plausible. Remember that, e.g., the magnetization at 4.2 K hardly depends on pressure up to $p = 20$ kbar in Fe$_3$Pt, while a considerable decrease is observed in Fe$_{65}$Ni$_{35}$ (see fig. 28). Analogously, 'hard' magnetic behavior is found in Fe$_3$Pt in the initial dependence of the magnetization on temperature (see inset in fig. 30) and in the magnetic contribution to the bulk modulus (see fig. 37), while in Fe$_{65}$Ni$_{35}$ we find magnetically 'soft' behavior in both properties. It is obviously more difficult to 'excite' Fe$_3$Pt out of the narrow minimum at the FM HS state and over the energy barrier into the LS state, than it is to drive Fe$_3$Ni up to the saddle point, i.e., out of the more shallow minimum at the HS state. Note also that, concerning experiments, we compare ordered Fe$_3$Pt with a disordered Fe$_{65}$Ni$_{35}$ alloy. Disorder very likely will lead to a decrease of the energy difference between the HS and LS state in the total energy curves and favour magnetic softness of Fe$_{65}$Ni$_{35}$ in comparison to ordered Fe$_3$Ni.

Finally, a convincing result concerning the concentration (or e/a) dependence
of the total energy in the FeNi system can be derived from the FSM calculations. It has been demonstrated earlier (Williams et al. 1983) that in ferromagnetic Fe$_{50}$Ni$_{50}$ (e/a = 9) the HS state at high volume is the ground state and there exists an energy difference of $\Delta E = E_{NM} - E_{HS} = 11.2$ mRy to the non-magnetic state at lower volume. We have also seen in fig. 44b that in comparison to Fe$_{50}$Ni$_{50}$ in fcc Fe the HS and NM states are energetically reversed, so that $\Delta E = E_{NM} - E_{HS} = -7.5$ mRy (Krasko 1987) or $\Delta E = -14.5$ mRy (Moruzzi et al. 1986). In figs. 50a–d we have sketched schematically the total-energy curves as a function of the radius of the Wigner–Seitz cell $r_w$ for the FeNi series. Note the reversal in level position just mentioned. In fig. 50e the energy difference $\Delta E = E_{NM} - E_{HS}$ is plotted versus the e/a ratio. The straight full line results when we use the Krasko (1987) value for $\Delta E$ in fcc Fe, the dashed line when we use the results of Moruzzi et al. (1986) (cf., fig. 44b). The dashed-dotted line shows $\Delta E$ versus e/a as originally proposed by Weiss (1963) for the FeNi system. The plus sign gives the result for $\Delta E$ in pure fcc Co (Moruzzi et al. 1986). To our feeling, the similarity between the ‘historic’ phenomenological Weiss model and the modern band calculations is striking. Although Weiss assumed the antiferromagnetic $\gamma_1$-state to be the ground state in pure fcc Fe and we have used here the NM state within the band model, it is clearly seen from the figure that, with increasing Ni concentration, in both models the energy difference reverses sign in the range e/a = 8.4–8.6. Consequently, for the Invar alloys – especially Fe$_{65}$Ni$_{35}$ with e/a = 8.7 – the FM HS state ($\gamma_2$-state in the Weiss model) becomes the ground state. Moreover, in the Invar range – as expected – the energy difference between HS and NM state (or HS and LS state) is small as compared to fcc FE or Fe$_{50}$Ni$_{50}$, so that the LS state is then thermally accessible from the ground state.

A special situation occurs when $\Delta E = 0$. The corresponding energy curves are shown schematically in fig. 50c. In this case it ‘costs’ no energy for the system to change (or fluctuate) between the ferromagnetic HS state and the paramagnetic or possibly antiferromagnetic NM (or LS) state. We call an alloy of this composition an ‘itinerant spin glass’, since FM and AF order are energetically equally possible. Note that in FeNi in the respective composition range (e/a = 8.6) mixed magnetic behavior (but not a pure SG phase) is indeed observed at low temperatures (cf., magnetic phase diagram in fig. 5). We have demonstrated in fig. 29 that in the range e/a = 8.3–8.4 the ordering temperatures of Invar systems in general become small, SG phases occur and the spontaneous volume magnetostriction $\omega_{so}$ (cf. fig. 23) vanishes at the respective compositions. We do not doubt that future total-energy calculations for other 3d-Invar systems will reveal these general features too.

In conclusion, the FSM calculations provide some new and comprehensive understandings of the ground state properties of Invar systems. In particular, the long debated difference between ‘hard magnetic’ Fe$_3$Pt and ‘soft magnetic’ Fe$_{65}$Ni$_{35}$ is explainable. There is no principal difference between the two Invar systems. Furthermore, some of the general features concerning the e/a or concentration dependence of Invar properties in the broad variety of systems presented in section 4 of this chapter can at least be made plausible. However,
Fig. 50. Total energy curves versus radius of the Wigner-Seitz cell for (a) Fe₅₀Ni₅₀ (Williams et al. 1983), (b) Fe₃Ni (Moruzzi 1988), and (d) pure fcc Fe (Moruzzi et al. 1986). Note the reversal in the relative position of HS and NM (or LS) state with change of the composition from Fe₅₀Ni₅₀ to pure fcc Fe. In (c), when both levels are at equal energy, an 'itinerant spin-glass' state occurs. (e) shows the energy difference between the NM (or LS) and HS states, \( \Delta E = E_{NM} - E_{HS} \), versus the electron concentration \( e/a \). The straight full line results, when the Krasko (1987) value of \( \Delta E \) is used for pure fcc Fe, the straight dashed line, when using the \( \Delta E \) value of Moruzzi et al. (1986). The dashed-dotted line shows \( \Delta E(e/a) \) as given by Weiss (1963). Note the striking similarity between the band-calculation results and the phenomenological Weiss model. The results also show that for Fe₅₀Ni₅₀ Invar \( \Delta E \) is small, of the order of 1–2 mRy, which means, the NM (or LS) state is thermally accessible from the HS ground state. The moment–volume instabilities, responsible for the Invar effect also drive the FeNi system into the martensitic \( \gamma \rightarrow \alpha \) phase transition around \( e/a = 8.65 \). As a consequence, neither the itinerant SG state nor the ordered Fe₃Ni phase can be reached experimentally in this system (cf. section 3.1.1 and fig. 5). Using the calculated value of \( \Delta E \) for pure fcc Co [plus sign in (e) after Moruzzi et al. (1986)] an analogous discussion could be carried through for the FeCo system, which is, however, not stable in the \( \gamma \)-phase.

caution is requested with respect to any interpretation at finite temperatures. The states connected with particular points on the binding surface (like the ones in fig. 48) represent states of the whole itinerant magnetic system. It is not known how lattice vibrations and spin disorder will change the energy surfaces when the temperature is increased. However, there are presently widespread theoretical activities to understand finite-temperature Invar properties on the basis of the
FSM method in connection with spin and density fluctuations (see table 8, 9.5.1–9.5.3).

6.2. Finite-temperature models

Early attempts to understand magnetic and magnetovolume effects of transition metals and alloys at finite temperatures have been scarce in the literature. A fundamentally new approach was first given by Moriya and Usami (1980) on the basis of the spin-fluctuation model for weak itinerant ferromagnets. Since Invar alloys are not WIF, this theory is not applicable to Invar. A rigid-band finite-\(T\) calculation by Hasegawa (1981) and an electron-phonon model by Kim (1982) could make some Invar properties at finite \(T\) plausible, but failed to explain the Invar features in detail.

A promising way to describe finite-temperature properties of Invar has been shown by Kakehashi (see, e.g., Kakehashi 1981–1985, 1988a and references therein) within the so-called 'local-environment theory'. The theory self-consistently takes into account the number of nearest-neighbor atomic and magnetic configurations in different systems at finite temperatures. Calculation of the amplitude of the local moments with respect to the atomic environment as a function of temperature, pressure, magnetic field and/or composition enabled Kakehashi to qualitatively explain a broad spectrum of Invar anomalies and magnetic as well as magnetovolume effects in several binary systems; so far, however, not for Fe\(_3\)Pt. Surprisingly, evidence for the existence of two distinct energy states in the high-temperature limit for, e.g., FeNi could not be given from these calculations. Moreover, the local-environment theory does not account for the typical features observed in Invar alloys in the temperature range \(T > T_c\). We show, e.g., in fig. 3 (dashed lines), the result of Kakehashi (1981) for the specific heat of FeNi in comparison to the experiments. The theoretical curves have been fitted at the respective experimentally determined Curie temperatures, since the absolute values computed theoretically are erroneous. Note that the second ‘bump’ in \(C_p(T)\) at temperatures below \(T_c\) is qualitatively correctly revealed by the calculations. On the other hand, the sudden drop in \(C_p(T)\) at \(T = T_c\) in the theoretical curves is not observed experimentally. Refinement of the LE approach for the understanding of the Invar effect thus also seems necessary in the future.

6.3. Evidence for high-spin–low-spin-state transitions from experiment

First experimental evidence for the existence of the HS–LS state transition has been given by us in investigations of the temperature dependence of the photoemission intensity on a single crystal of ordered Fe\(_3\)Pt (Kisker et al. 1987a,b). In fig. 51a we show the spin-integrated energy distribution curves as measured below \(T_c = 450\) K for Fe\(_3\)Pt at \(T = 270\) K \((T/T_c = 0.6)\) and above \(T_c\) at \(T/T_c = 1.22\). As shown in fig. 51b, the data taken below \(T_c\) differ from the data above \(T_c\) by a significant decrease in intensity within an energy range of about 0.4 eV below \(E_F\), and an increase in intensity within an energy range of about 0.5 eV above \(E_F\).
Fig. 51. (a) Spin-integrated energy-distribution curves from Fe₃Pt(001) for normal emission and s-polarized light at $h\nu = 60 \text{ eV}$ as determined at $T = 270 \text{ K} = 0.6T_c$ (full curve) and $T = 500 \text{ K} = 1.22T_c$ (dashed dotted curve). The intensities are normalized to the photon flux (Kisker et al. 1987a). (b) Difference between the EDCs of (a) taken at 500 K (low-spin state) and 270 K (high-spin state) (dots and full line). The dashed line is the theoretically calculated DOS difference for fcc Fe at $r_{ws} = 2.68 \text{ a.u.}$ in the LS (cf. fig. 52c) and HS state (cf. fig. 52d), convoluted with a 0.4 eV FWHM Gaussian-type resolution function (after Podgorny 1989).

while at $E_F$ the intensity does not change. We attribute these features to the flat band with $\Delta_2$ symmetry, which, in the HS state for $T \leq T_c$, is found at about 0.4 eV below $E_F$, but in the LS state about 0.2 eV above $E_F$, because the increase in intensity above $E_F$ is an order of magnitude larger than expected from a variation of the Fermi function $f(E, T)$ with temperature alone.

As we have shown earlier (Carbone et al. 1987), because of symmetry reasons the band structure of fcc Fe in the X-W direction and the band structure of Fe₃Pt in the $\Gamma$–X direction correspond to each other. Therefore, we can compare the DOS for pure fcc Fe in the HS and LS states with our results of the photoemission on Fe₃Pt. Figures 52a and b gives the total (up and down spin) DOS for fcc Fe in the LS and HS states, respectively, as calculated very recently by Podgorny (1989) for a radius of the Wigner–Seitz cell $r_{ws} = 2.68 \text{ a.u.}$ Analogous features, i.e., the high DOS peak closely below $E_F$ in the HS state and slightly above $E_F$ in the LS state, are found in theoretical calculations for Fe₃Ni and Fe₃Pt (Podgorny 1988) as well.
If one subtracts from the total DOS in figs. 52a and b the effect of the Fermi function \( f(E, T) \) at the respective experimental temperatures (\( T = 270 \text{ K} \) for the HS state, \( T = 550 \text{ K} \) for the LS state) this results in the DOS minus \( f(E, T) \) distributions curves shown in figs. 52c and d. The difference of these two distribution curves convoluted with the experimental resolution function (0.4 eV FWHM), results in the dashed line shown in fig. 51b. One can see that the agreement between the theoretically calculated DOS difference for fcc Fe and the experimentally (from fig. 51a) determined intensity difference between the LS and HS states of Fe\(_3\)Pt is very good, suggesting that they are of the same physical origin. We therefore conclude that we have given clear experimental evidence for the occurrence of the high-spin–low-spin-state transition in Fe\(_3\)Pt Invar with temperature. This volume-coupled transition, to our feeling, is the salient feature of Invar.

The amplitude of the intensity above \( E_F \) in photoemission curves should be a measure for the weight of the low-spin state if the interpretation given applies. As shown by Holden et al. (1984) the fractional change of the radius of the Wigner–Seitz cell with temperature, i.e., the fractional linear expansion \( \Delta l/l = (l(T) - l(0))/l(0) \), is proportional to the change of the square of the local magnetic moment with temperature, \( m^2(T) - m^2(0) \), where \( T \) is an elevated temperature \( T > T_C \). Therefore, the square of the intensity above \( E_F \) in the EDCs, \( I^2(T) \), should be proportional to \( m^2(T) \) which is proportional to the volume change \( \omega_v = (\Delta V/V)(T) \). In fig. 53 we have plotted the experimentally
determined squared intensity $I^2$ (dashed line) as a function of temperature together with the behavior of the negative spontaneous volume magnetostriction $\omega_s(T)$ as measured by Sumiyama et al. (1979) for ordered Fe$_3$Pt. Also plotted in fig. 53 is the spin polarization as determined by us experimentally on our Fe$_3$Pt sample (actual concentration Fe$_{72}$Pt$_{28}$) as a function of temperature, leading to a $T_C$ value of 450 K, which corresponds to a degree of order of 60–70%. One can see that in the range where the polarization starts to decrease, both $I^2(T)$ and $-\omega_s(T)$ increase in the same way. This gives further support for the correctness of our analysis, and the presence of the high-spin–low-spin transitions in Fe$_3$Pt on approach to $T_C$ as well as on passing through $T_C$.

Our experimental XPS-results (fig. 51) on Fe$_3$Pt have recently been rediscussed from a theoretical point of view concerning controversial aspects. On the one hand, it was quoted (Kakehashi 1988b) that the DOS-difference curve (fig. 51b) is in better agreement with curves obtained from the transition from a strong-band ferromagnetic state at $T < T_C$ to disordered local-moment states (DLM) with considerable large local moments at $T > T_C$. On the other hand, this was put into doubt by calculations of Gollisch and Feder (1989), who showed that the magnetic structure of Fe$_3$Pt Invar at 1.2 $T_C$ is characterized by large local-moments, however, with a substantial amount of magnetic SRO. This was also shown to be valid for pure bcc Fe, for which around $T_C$ a ferromagnetic SRO extending over 4 to 6 Å was reported (Haines et al. 1985), ruling out the validity
of the DLM picture. Further work on photoemission, both theoretical and experimental, is obviously necessary.

Very recently, a further convincing experimental proof for the existence of HS–LS state transitions in Fe$_{68}$Ni$_{32}$ and ordered and disordered Fe$_{72}$Pt$_{28}$ Invar has been given in measurements of the pressure dependence of the Mössbauer effect by Abd-Elmeguid et al. (1988) and Abd-Elmeguid and Micklitz (1989). Figure 54a shows their result of the pressure dependence of the normalized average effective hyperfine field $[B_{\text{eff}}(p)/B_{\text{eff}}(0)]$ as measured at 4.2 K on these Invar alloys. Note that in accordance with the results of the FSM calculations in figs. 48 and 49, $B_{\text{eff}}$ of Fe$_{68}$Ni$_{32}$ initially decreases continuously on the application of pressure. The decrease in $B_{\text{eff}}$ or magnetic moment sets in immediately with increasing $p$, driving the system out of the HS state through the reduction of lattice volume. At $p = 6$ GPa, $B_{\text{eff}}(p)/B_{\text{eff}}(0)$ starts to drop faster and at $p_c \approx 7$ GPa the LS state is reached, supported by the observation that for $p > p_c$.

![Diagram](image_url)

Fig. 54. (a) Average effective hyperfine field at pressure $p$, $B_{\text{eff}}(p)$, normalized to $B_{\text{eff}}$ at $p = 0$ versus pressure $p$ (in GPa) for disordered Fe$_{68.5}$Ni$_{31.5}$ and ordered and disordered Fe$_{72}$Pt$_{28}$ Invar as determined from Mössbauer experiments at 4.2 K (after Abd-Elmeguid et al. 1988 and Abd-Elmeguid and Micklitz 1989). Salient general feature is the experimental proof for the occurrence of HS–LS state transitions induced by pressure in all three alloys. Details can be quantitatively understood within the results of the FSM calculations (cf., figs. 48, 49). (b) Relative change of the Curie temperature $T_c(p)/T(p = 0)$ versus pressure for the same samples as in (a).
$B_{\text{eff}}(p)/B_{\text{eff}}(0) \approx \text{const.}$ The residual value of the effective moment in the LS state is $\mu = 0.6\mu_B$ in accordance with the theoretical value (cf. fig. 49a).

The behavior of the 'soft' magnetic material Fe$_{68}$Ni$_{32}$ is contrasted by the 'hard' magnetic behavior of ordered Fe$_{72}$Pt$_{28}$. We observe in fig. 54a that a critical pressure $p_c = 4$ GPa is necessary before this alloy can be driven out of the HS state with pressure, reflecting the deep energy-valley around the HS state revealed by the FSM calculations (cf., fig. 49b). For $p > p_c$ the moment of ordered Fe$_3$Pt then drops continuously until for $p \geq 7$ GPa the LS state is reached. As expected from a comparison with the results in figs. 48a and b, the residual moment of ordered Fe$_{72}$Pt$_{28}$ in the LS state is much higher than in Fe$_{65}$Ni$_{35}$, although the absolute value of $\mu = 1.6\mu_B$ for the LS state of ordered Fe$_{72}$Pt$_{28}$ is only in qualitative agreement with the result given for ordered Fe$_3$Pt by the calculation (cf., fig. 48b). As expected, disordered Fe$_{72}$Pt$_{28}$ takes an intermediate position between the 'soft' magnetic Fe$_{68}$Ni$_{32}$ and the 'hard' magnetic ordered Fe$_{72}$Pt$_{28}$. As can be seen from fig. 54a, at a critical pressure $p_c = 2$ GPa the reduction of the moment sets in for disordered Fe$_{72}$Pt$_{28}$, and at around $p > 7$ GPa the LS state is reached with a residual moment of $\mu_{Fe} = 1.0\mu_B$. Unfortunately, no FSM calculations for disordered systems are presently available to allow further quantitative analysis.

The reduction in Curie temperatures accompanying the HS–LS transitions are demonstrated in fig. 54b, where the normalized Curie temperatures $T_c(p)/T_c(0)$ versus pressure are plotted. Although the overall behavior is similar for the three Invar systems, note again the magnetic hardness of Fe$_{72}$Pt$_{28}$ (cf., also fig. 28).

In conclusion, the experimental results presented in this section to our feeling give clear evidence for the presence of HS–LS state transitions in Invar alloys, simultaneously supporting the results of the FSM calculations.

7. Conclusions and outlook

If we assume that in an itinerant ferromagnet, in general, there are short-ranged magnetic correlations — or longitudinal and/or transverse spin fluctuations — in the temperature range around and above $T_c$, we can ask the question, what is the reason for all the differences observed between the physical behavior of Invar and ordinary ferromagnets? To our feeling, the principal answer is as follows. Although there are moment–volume instabilities, characterized by high–spin (large volume), low–spin (small volume) or no-spin (small volume) states present in many pure 3d-elements, alloys or compounds, the essential feature is that in Invar the energy difference $\Delta E$ between the states is so small that the states become thermally accessible via low-energy excitations. Experiments (section 4) and band calculations (figs. 49 and 50) have shown that indeed Invar behavior — i.e., maximum magnetovolume effects — occur, when $\Delta E$ is of the order of 1–2 mRy or 150–300 K. Clearly, the population of the states or their volume fraction is temperature dependent. Thus magnetovolume contributions — though small — initiate from zero temperature, but drastically increase in size, when $kT \sim \Delta E$, as seen, e.g., in the dependence of $\omega_q(T)$ (cf., fig. 53) or the magnetic
contribution to the bulk modulus $\Delta B_m(T)$ (cf., fig. 37). With increasing temperature, i.e., rising excitations of phonons, it also becomes possible that, vice versa, density fluctuations produce magnetic fluctuations in Invar through the strong magnetoelastic coupling (large magnetic Grüneisen parameter). This stems from the observation that the (equilibrium) volume difference between HS and LS (or NM) states is of the same order of magnitude (3–5%, cf., fig. 49) as thermal volume fluctuations (Renaud 1988). We are thus bound to assume that the unusual fluctuations observed in the high-temperature range of the specific heat (cf., figs. 3 and 41) find their origin in these density fluctuations, causing local magnetic fluctuations. This is supported by the fact that in non-Invar ferromagnets these high-temperature ‘oscillations’ in $C_p(T)$ are not observed (Pepperhoff 1989), since the energy differences between the instability states – if they exist – are too large.

Concerning the change of the energy difference between the instability levels $\Delta E$ with temperature, no reliable answer has been given so far on the basis of the theoretical FSM calculations. Again, we can only guess what happens. It is possible that the negative anharmonicity which is apparent only at low temperature in Invar systems, eventually becomes a positive anharmonicity at high temperatures. This would imply that:

(i) at a certain temperature HS, LS and NM states have the same energy ($\Delta E = 0$), and it ‘costs’ no energy to go from one to the other. This could explain the absence of an ordering peak in the specific heat at $T_C$ (or $T_N$) (cf. figs. 41, 42) if $T_C$ (or $T_N$) is identified with this ‘certain temperature’. If then

(ii) at even higher temperatures the binding curves become skewed towards high volumes (positive anharmonicity) then the LS state will be the ground state. Transitions from the LS (or NM) to the HS state then lead to the reappearance of magnetovolume effects in the paramagnetic range of an Invar alloy, which has indeed been observed experimentally (see figs. 19–21 and 42).

As we have seen, the larger on many occasions in this chapter, large magnetovolume effects (Invar) are observed as a function of concentration ($e/a$) shortly before the systems undergo a structural first-order transition from the fcc $\gamma$- into the bcc $\alpha$- phase at some smaller $e/a$-values as compared to the Invar range. Note that the $\gamma-\alpha$ transition is accompanied by a large increase in volume, from dense packed fcc to the much more open bcc structure. As we have seen, the larger the magnetovolume effects become, the smaller the energy difference $\Delta E$ between HS and LS states gets. Now $\Delta E$ decreases with decreasing $e/a$, as, e.g., shown for the FeNi system in fig. 50e. Therefore, one has the impression that at some (certainly system dependent) $e/a$ value the positive volume magnetostriction would become so large that the system ‘prefers’ to undergo the $\gamma-\alpha$ structural phase transition. Note that in FeNi at zero temperature this happens at $e/a = 8.65$ (cf. fig. 50e). If Mn, with a large atomic volume, is alloyed to FeNi, the structural phase transition does not occur. Instead, $\Delta E$ can get increasingly smaller so that around $e/a = 8.4$ for $\Delta E = 0$ the itinerant spin-glass phase is observed [see inset of fig. 19 and also Wassermann (1989a)] and then for $e/a < 8.4$ in $Fe_{65}Ni_xMn_{35-x}$ we find antiferromagnetic Invar.
In total, in our opinion, the particular binding-energy surfaces computed at \( T = 0 \) for 3d-elements and alloys, and revealing the existence of certain local minima with corresponding fixed magnetic moments and atomic volumes, provide a new and general basis for the understanding of the large magnetovolume effects observed in these systems. To our feeling, the structural phase-transitions equally characteristic for 3d-elements (allotropy) and alloys are also ultimately connected to the peculiarities of these binding-energy surfaces. Certainly, more theoretical and experimental work is necessary to understand the properties of the systems at finite temperatures and – equally important – antiferromagnetic Invar.

Acknowledgement

I am very much indebted to the late Peter Wohlfarth, who originally encouraged me to write this chapter. My thanks also go to W. Pepperhoff for many valuable discussions and sublet of unpublished data. Helpful discussions with Y. Nakamura and V. Moruzzi and my own co-workers M. Acet, G. Lecomte and W. Stamm are also gratefully acknowledged. Finally, I thank M.M. Abd-Elmeguid for allowing me to use his pressure data prior to publication, and J. Kästner for critically reading the manuscript. The work has been supported within Sonderforschungsbereich 166 Duisburg-Bochum.

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