Compressibility of YMn$_2$, Y$_6$Mn$_{23}$, YMn$_{12}$ and ScMn$_2$ studied by synchrotron powder diffraction

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Abstract. The compressibility of manganese compounds with different structures and compositions (YMn$_2$, Y$_6$Mn$_{23}$, YMn$_{12}$, Y(Mn$_{0.8}$Fe$_{0.2}$)$_2$ and ScMn$_2$) was studied up to $\approx$40 GPa using a diamond anvil cell with synchrotron radiation.

In the case of YMn$_2$ we observed a very large compressibility which decreases considerably upon changing the atomic surrounding of the Mn atoms, as shown by the pseudobinary Y(Mn$_{0.8}$Fe$_{0.2}$)$_2$ and ScMn$_2$. The other two Y–Mn compounds Y$_6$Mn$_{23}$ and YMn$_{12}$ also show enhanced compressibilities; however, they are not as large as that of YMn$_2$.

Thermal expansion data, which were also included in the discussion, show that the thermal expansion is closely related to the compressibility. The unusually large differences in the compressibility and the thermal expansion among the compounds investigated have been attributed to a different 'chemical pressure' acting on the Mn atoms, depending on the space available on the Mn sites in the different structures.

1. Introduction

Comparing the properties of the intermetallic compounds consisting of rare-earth elements (R) and 3d metals (M = Mn, Fe, Co, Ni), it is found that the compounds with M = Mn very frequently exhibit the most complex physical properties among them, especially if their magnetic properties are considered. For example, it has been found that in the RMn$_2$ compounds with the light rare earths or Y, the Mn ions bear magnetic moments, whereas in the compounds with the heavy rare earths, no intrinsic Mn moments exist. This difference in the magnetic behaviour of Mn is due to the different Mn–Mn distance, which is smaller in the heavy RMn$_2$ compounds.

Investigations of the three Y–Mn compounds YMn$_2$, Y$_6$Mn$_{23}$, YMn$_{12}$ (see e.g. the review [1] and [2, 3]) and related pseudobinaries, such as Y(Mn, Fe)$_2$ [4–6], Y$_6$(Mn, Fe)$_{23}$ [7, 8] and (Y, Sc)Mn$_2$ [9], show that the magnetic properties of the Mn atoms depend sensitively on:

 (a) the atomic surrounding,
 (b) an external or a chemical pressure and
 (c) the magnetic state of the rare-earth partner elements.

The outstanding behaviour of these Mn-based compounds is especially reflected by the thermal expansion, which has been investigated in detail for YMn$_2$, Y$_6$Mn$_{23}$, YMn$_{12}$ [3], Y(Mn$_{1-x}$Fe$_x$)$_2$ [6] and Y$_6$(Mn$_{1-x}$Fe$_x$)$_{23}$ [8].

In the following a brief summary of the structural and magnetic properties which characterize the Y–Mn compounds will be given.

1.1. YMn₂

This is the most intensively investigated compound among the three Y–Mn compounds. It crystallizes in the C15 (cubic Laves phase) structure with a lattice parameter of 7.684 Å at room temperature and ambient pressure. It shows a first-order transition from paramagnetism to an antiferromagnetic state of the Mn sublattice [10] with a large thermal hysteresis (roughly 20 K) at the Néel temperature ($T_N = 90$ K). This compound is also known for the existence of strong spin fluctuations (see e.g. [11] and references therein) and for a huge volume expansion ($\Delta V / V$ is about 5%) accompanying the onset of magnetism [12, 13]. Below T_N the linear thermal expansion coefficient $\alpha(T)$ is about zero, but it takes values of nearly 50×10^{-6} K^{-1} within a few tenths of a degree above T_N and reaches its maximum value of about 55×10^{-6} K^{-1} at around 350 K. This value is about four times larger than the α-values measured for comparable isostructural compounds, such as YFe₂, YNi₂ and also YCo₂ (see figure 2 in [3]). Magnetic measurements under pressure showed that $\partial T_N / \partial P$ is negative and exceptionally large. The antiferromagnetic order becomes suppressed at pressures above 0.37 GPa [14] or by small levels of substitution of Fe for Mn [4, 5] as well as of Lu or Sc for Y [9, 15]

For the discussion of the properties of YMn₂ we included in our pressure investigation a sample with $x = 0.2$ from the pseudobinary series Y(Mn₁₋ₓFeₓ)₂ which is paramagnetic down to the lowest temperatures and shows a reduced thermal expansion over the whole temperature range [6]. Another Mn-based compound which has been included in the pressure studies is ScMn₂ which crystallizes in the hexagonal Laves phase C14 (very similar to C15). In this compound the available space at ambient pressure for the Mn ion is considerably reduced because of the smaller ionic radius of Sc.

Furthermore, thermal expansion measurements of ScMn₂ and of UAl₂, which is known as a classical spin-fluctuation system, were also performed and included in the discussion.

1.2. Y₆Mn₂₃

This is the compound with the most complicated atomic arrangement in the unit cell among the three systems investigated. It crystallizes in the cubic Th₆Mn₂₃-type structure with four non-equivalent crystallographic sites for the Mn atoms and with a unit-cell volume roughly five times larger than that of the others. Altogether there are 116 atoms in the cubic unit cell with the lattice constant $a = 12.45$ Å (at room temperature and ambient pressure). Another feature which distinguishes this compound from the others is its very high magnetic ordering temperature $T_C = 486$ K [16]. Thermal expansion measurements of Y₆Mn₂₃ [3] and of compounds from the pseudobinary Y₆(Mn₁₋ₓFeₓ)₂₃ series [8] showed that on the Mn-rich side the thermal expansion and the magnetovolume effect are much larger than on the Fe-rich side. However, this enhanced thermal expansion on the Mn-rich side appears only at elevated temperatures in the paramagnetic range. The α-value reaches almost 50×10^{-6} K^{-1} at around 800 K but it becomes rapidly suppressed when substituting Fe for Mn, which is similar to what has been observed in the case of YMn₂ [6].

1.3. YMn₁₂

This compound is the only one among the three with a non-cubic unit cell. It crystallizes in the tetragonal ThMn₁₂-type structure with three non-equivalent Mn sites with $a = 8.615$ Å

and $c = 4.757$ Å at room temperature and ambient pressure. It orders antiferromagnetically below 110 K [1]. As in the case of YMn_2 and Y_6Mn_{23}, there is an enhanced linear thermal expansion in the paramagnetic range ($\alpha = 24 \times 10^{-6}$ K^{-1} at 300 K and 50×10^{-6} K^{-1} at around 800 K) [3].

The aim of the present study was to investigate the influence of an external pressure on the unit-cell volume of the compounds mentioned above, since we expected from compressibility measurements a better understanding of the question concerning the electronic stability of Mn in the different surroundings in the different structures.

2. Experimental procedure

Polycrystalline samples of YMn_2, $Y(Mn_{0.8}Fe_{0.2})_2$, Y_6Mn_{23}, YMn_{12}, $ScMn_2$ and UAl_2 were melted in an induction furnace in a water-cooled copper boat from raw materials with a purity equal to or better than 3N. Subsequently the ingots were wrapped in tantalum foils, placed in evacuated quartz glass tubes and annealed at temperatures and for time periods adequate for the different sample materials. X-ray structure analysis showed that the foreign phase content was less than 2% in all compounds, except in YMn_{12}, where a few per cent of elementary Mn were found. However, this Mn impurity was no problem as regards measuring the temperature and pressure dependence of the lattice parameters of YMn_{12} in x-ray diffraction experiments.

The crystal structures of the compounds are: for YMn_2, $Y(Mn_{0.8}Fe_{0.2})_2$ and UAl_2: $MgCu_2$-type structure (cubic Laves phase C15); for $ScMn_2$: hexagonal Laves phase C14; for Y_6Mn_{23}: cubic Th_6Mn_{23}-type structure; and for YMn_{12}: tetragonal $ThMn_{12}$-type structure.

The pressure experiments were performed at room temperature using a Syassen–Holzapfel-type diamond anvil cell [17] within the following pressure ranges: YMn_2: 0–40 GPa; $Y(Mn_{0.8}Fe_{0.2})_2$: 0–42 GPa; Y_6Mn_{23}: 0–48 GPa; YMn_{12}: 0–20 GPa; and $ScMn_2$: 0–10 GPa. Fine-powder samples were loaded into a 0.2 mm hole drilled into an annealed (800 °C for three hours) and pre-indented Inconel X750 gasket together with a ruby chip (for pressure determination by the ruby fluorescence method) or quartz powder as the pressure marker. Silicone oil or a 4:1 methanol–ethanol mixture was used as the pressure-transmitting medium. No structural phase transitions were observed in any of the samples. The experiments were performed at the energy-dispersive synchrotron radiation diffraction facility (F3 beamline) of the storage ring DORIS III of HASYLAB (DESY, Hamburg) and at the x-ray diffraction beamline of ELETTRA (Trieste) with an image plate detector.

For the determination of the bulk modulus (K_0) and its first derivative with respect to pressure (K_0') we fitted the Murnaghan equation of state (EOS) to the experimentally obtained volume versus pressure data up to pressures of about 10 GPa. The reason for this restriction to lower pressures in the quantitative analysis is that both of the pressure-transmitting media used become solid roughly above 10 GPa, i.e. the pressure becomes non-hydrostatic at higher pressures, which causes errors in the determination of the volume as well as the determination of the pressure (due to broadened x-ray and ruby fluorescence lines). In order to estimate the uncertainties of K_0 and K_0', we carried out the EOS fit procedure for various pressure ranges below 10 GPa and made a comparison with the results obtained using other EOS models (e.g. the Birch model).

The thermal expansion of UAl_2 and $ScMn_2$ was determined by x-ray diffraction experiments with a He-flow cryostat suitable for temperatures from 4.2 K to 450 K.

3. Results and discussion

3.1. YMn$_2$

Figure 1 shows the normalized change of the unit-cell volume for YMn$_2$, Y(Mn$_{0.8}$Fe$_{0.2}$)$_2$ and ScMn$_2$ for pressures up to about 40 GPa. (The inset shows the variation of the hexagonal lattice parameters of ScMn$_2$; the other two systems are cubic.) To quantify the compressibility for a comparison among the three compounds and with values given in the literature, we fitted the Murnaghan equation of state (EOS) [18] to the experimental data. The full curves in figure 1 show the results from the fit procedure for the pressure range up to 10 GPa. The values obtained for the bulk modulus K_0 ($1/K_0 = -\partial \ln V/\partial P$) and its first derivative (with respect to pressure) K_0' are listed in table 1. The K_0-value of YMn$_2$ (19 GPa) is in agreement with the value of 16 GPa previously obtained from neutron diffraction measurements up to 0.3 GPa between 2 and 190 K [19]. The extremely small K_0-value of YMn$_2$ indicates an extraordinary
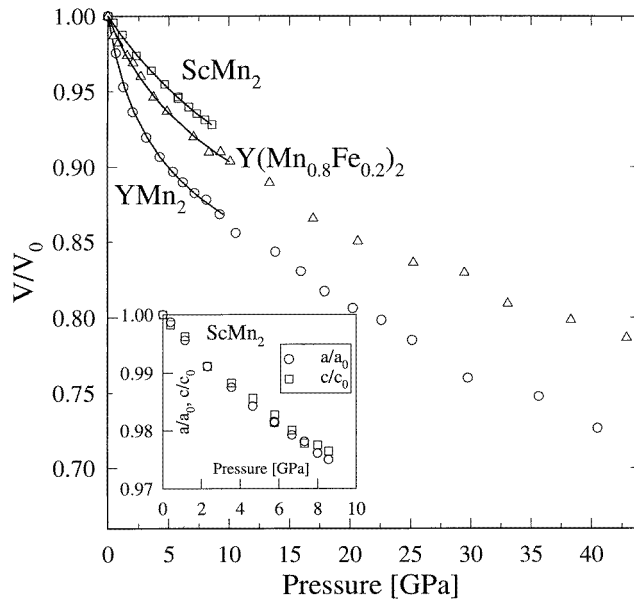

Figure 1. The pressure dependence of the normalized unit-cell volume for YMn$_2$, Y(Mn$_{0.8}$Fe$_{0.2}$)$_2$ and ScMn$_2$ obtained from powder diffraction synchrotron experiments at room temperature. The symbols indicate the experimental results; the full curves represent a fit of the Murnaghan EOS. The inset shows the variation of the hexagonal lattice parameters of ScMn$_2$.

Table 1. The K_0- and K_0'-values obtained by fitting the Murnaghan EOS to the experimental data; the corresponding linear thermal expansion coefficients at 300 K and ambient pressure are also shown.

	K_0 at 300 K	K_0' at 300 K	α at 300 K and 0 GPa
YMn$_2$	19.0 ± 1.0 GPa	15.2 ± 1.5	54×10^{-6} K^{-1} [3]
ScMn$_2$	80 ± 4 GPa	9.0 ± 0.9	$(14.0 \pm 0.5) \times 10^{-6}$ K^{-1}
Y(Mn$_{0.8}$Fe$_{0.2}$)$_2$	47 ± 2 GPa	13.2 ± 1.4	30×10^{-6} K^{-1} [6]
Y$_6$Mn$_{23}$	39 ± 2 GPa	15.8 ± 1.7	$(16 \times 10^{-6}$ K$^{-1})^a$ [3]
YMn$_{12}$	84 ± 4 GPa	13.5 ± 1.0	24×10^{-6} K^{-1} [3]

[a] Y$_6$Mn$_{23}$ is magnetically ordered at 300 K and ambient pressure.

large compressibility, which is somewhat reduced for the substituted sample; however, a value of $K_0 = 47$ GPa still means a large compressibility. Usually K_0-values for lanthanide or actinide intermetallics are found between about 50 GPa and 300 GPa, and K_0'-values between 4 and 8 (see e.g. the review [20]). Interestingly the values for $ScMn_2$ are almost within this range.
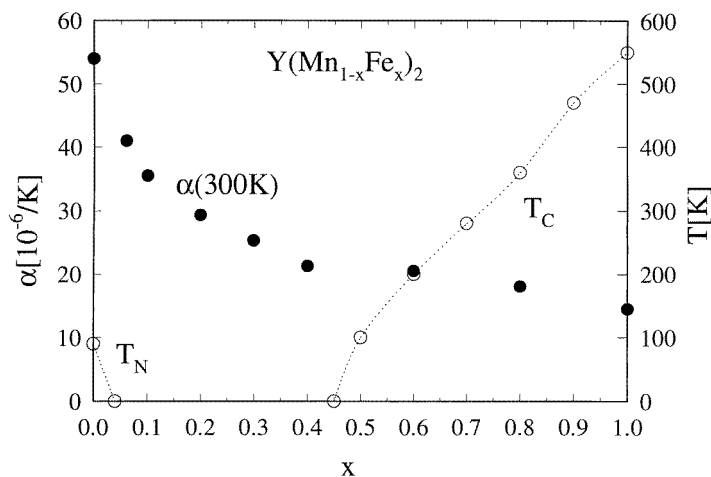
Figure 2. The variation of the linear thermal expansion coefficient α for the $Y(Mn_{1-x}Fe_x)_2$ series [6] at room temperature (300 K). The variation of the magnetic ordering temperatures T_N and T_C with concentration is depicted by the open symbols.

The large compressibility of the two Y-based compounds YMn_2 and $Y(Mn_{0.8}Fe_{0.2})_2$ is intimately related to their thermal expansion behaviour. In figure 2 the linear thermal expansion coefficient α ($=d(\Delta l/l)/dT$) at 300 K is shown for the whole pseudobinary series [6]. $\alpha(x)$ decreases non-linearly with increasing Fe concentration to a value of 15×10^{-6} K^{-1} for YFe_2. This value is about the same as for the isostructural compounds YCo_2 and YNi_2 (see e.g. [3]). For $Y(Mn_{0.8}Fe_{0.2})_2$ the linear thermal expansion is still enhanced ($\alpha(300$ K$) = 30 \times 10^{-6}$ K^{-1}); however, it is smaller than that of YMn_2 ($\alpha(300$ K$) = 54 \times 10^{-6}$ K^{-1}).

From these data it is obvious that

(a) the outstanding large compressibility and the thermal expansion are closely related and
(b) both are basically determined by the Mn sublattice.

On the other hand the behaviour of the Mn ions depends on the space in a given structure and the environment.

Note that the available space in $ScMn_2$ is much smaller than that in YMn_2: $ScMn_2$ crystallizes in the hexagonal C14 structure, which is only slightly different from the C15 structure. The pseudocubic lattice parameter determined for $ScMn_2$ at room temperature and ambient pressure gives $a_0 = 7.130$ Å which is much smaller than that of YMn_2 ($a_0 = 7.684$ Å). The difference in the volume per f.u. of about 20% means that the Mn tetrahedra are strongly compressed in $ScMn_2$. This 'chemical' pressure in $ScMn_2$ leads to a considerably reduced compressibility (reflected by the corresponding values of K_0 and K_0'; see table 1) and also to a normal linear thermal expansion ($\alpha = (14.0 \pm 0.5) \times 10^{-6}$ K^{-1} at 300 K, determined within the present study).

The sensitivity of the Mn atoms to a chemical pressure (e.g. by substituting Sc for Y) is confirmed by a comparison with other Laves phase compounds of Y with Fe, Co and Ni,
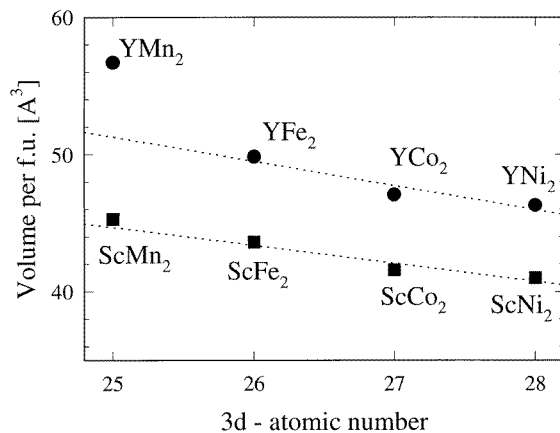
Figure 3. The volume per formula unit for YT_2 and ScT_2 compounds with T = Mn, Fe, Co and Ni. The dashed lines represent linear regressions to the values for T = Fe, Co, Ni.

which are the neighbours of Mn in the periodic table: in figure 3 the volumes per f.u. at ambient pressure and room temperature of YMn_2, YFe_2, YCo_2 and YNi_2 are compared with the values for the corresponding compounds with Sc. As can be seen from this figure, the replacement of Y with Sc leads to a volume reduction in all three compounds; however, in the case of YMn_2 this volume collapse is almost twice as large.

3.2. Y_6Mn_{23}

Figure 4 shows the normalized variation of the unit-cell volume of Y_6Mn_{23} in the pressure range up to 48 GPa. There is also an enhanced compressibility, which is comparable to that of $Y(Mn_{0.8}Fe_{0.2})_2$. The curve in figure 4 again represents a fit of the Murnaghan EOS to the experimental data up to 10 GPa. The values obtained for the bulk modulus and its first pressure derivative are listed in table 1. The value of K_0' is nearly the same as that of YMn_2. The value of K_0 is not as small as that of YMn_2; however, it is still much smaller than the values for most
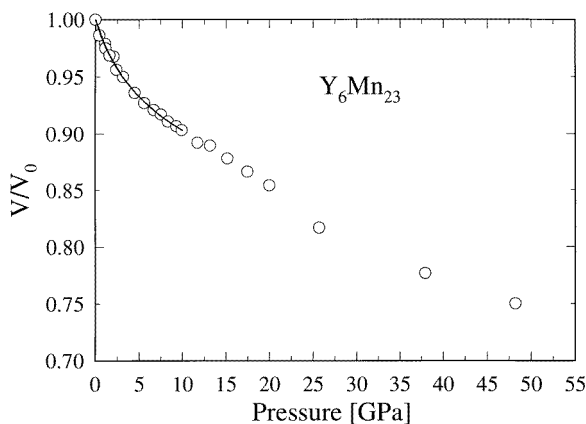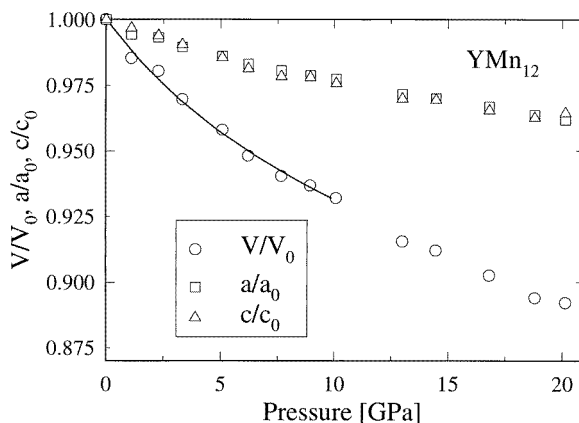

Figure 4. The pressure dependence of the normalized unit-cell volume of Y_6Mn_{23} obtained from powder diffraction synchrotron experiments at room temperature.

of the intermetallics reported in [20].

There is however one circumstance which makes a discussion of the data more difficult: Y_6Mn_{23} is magnetically ordered at room temperature and ambient pressure ($T_C = 486$ K). This is important because the thermal expansion of itinerant magnetic compounds (e.g. compounds for which the magnetism is basically due to 3d electrons) is usually smaller below T_C than in the paramagnetic state. The reason for this is the magnetoelastic coupling, which causes a positive contribution to the volume in the ordered state (see e.g. the review article [21]). An estimation of this magnetovolume effect obtained by extrapolating the thermal expansion from above T_C [3, 8] gives a value of roughly 1.5% at room temperature, where the pressure experiments have been performed. If now the magnetic ordering is shifted below room temperature by external pressure, the compressibility will be additionally enhanced by the suppression of this magnetovolume effect. Assuming that dT_N/dP is of the same order of magnitude as for YMn_2 (in [22], values for $\partial T_N/\partial P$ for YMn_2 from -10 to -34 K kbar^{-1} are reported), the magnetic ordering in Y_6Mn_{23} at room temperature should be suppressed at pressures of a few GPa.

3.3. YMn₁₂

The normalized unit-cell volume and the lattice parameters a, c of YMn_{12} for pressures up to 20 GPa are given in figure 5. The lattice parameters a and c exhibit the same pressure dependence, i.e. the compression of the unit cell with pressure is isotropic. The curve in the figure represents the fit of the Murnaghan EOS to the data points below 10 GPa. The values obtained for the bulk modulus and its first pressure derivative are listed in table 1. The large value of K_0' is enhanced like those of YMn_2, $Y(Mn_{0.8}Fe_{0.2})_2$ and Y_6Mn_{23}, whereas the value for K_0 fits into the sequence of other intermetallic compounds.


Figure 5. The pressure dependence of the normalized unit-cell volume and of the tetragonal lattice parameters of YMn_{12} obtained from powder diffraction synchrotron experiments at room temperature.

4. Conclusion and summary

In table 1 the values for K_0 and K_0' as well as the linear thermal expansion coefficients α at 300 K and ambient pressure are summarized for all of the Y–Mn compounds investigated and $ScMn_2$. In order to illustrate the correlation of the compressibility values ($1/K_0$) and the linear
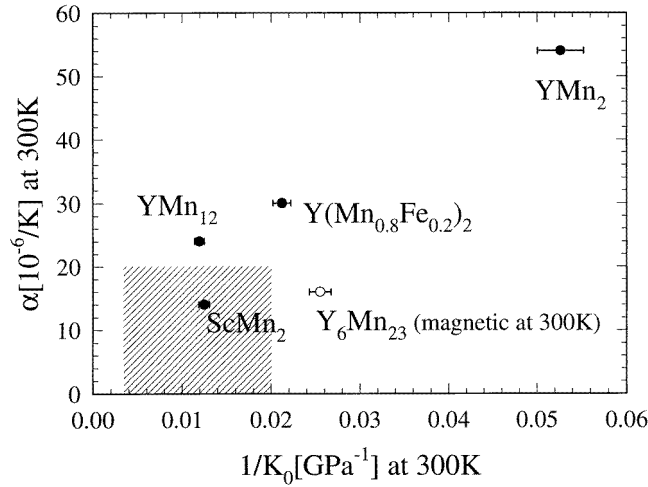
Figure 6. Comparison of the linear thermal expansion coefficient α and the compressibility at 300 K for all investigated Mn based compounds. The shaded area indicates the range where normal intermetallics would be located in this presentation. The error bars for α and some of the values of $1/K_0$ lie within the symbol size.

thermal expansion coefficients (α), both quantities are depicted in one diagram in figure 6. The corresponding value for Y_6Mn_{23} is denoted by an open symbol, in order to emphasize that this compound is magnetically ordered at 300 K and ambient pressure ($T_C = 486$ K), which means that due to the magnetoelastic effect the α-value is reduced and the compressibility is enhanced (if the magnetic ordering is suppressed by pressure).

The shaded region in figure 6 indicates the range of the compressibility values of all of the intermetallics with lanthanides or actinides, reviewed in [20], as well as the upper limit for the thermal expansion at 300 K for comparable intermetallic compounds without Mn [3, 6]. As can be seen from this figure, all of the Y–Mn compounds investigated lie outside the shaded region; however, most remarkable is the position of YMn_2. Furthermore, it is obvious that there is a correlation between the thermal expansion and the compressibility, which has to be expected from simple theoretical considerations, since in a first approximation the compressibility appears as a prefactor in the corresponding terms of the thermal expansion (see for instance [23]).

The results can be summarized as follows:

(a) Rare-earth intermetallics with Mn as partner element differ in many of their physical properties from rare-earth intermetallics with other 3d elements (such as Fe, Co or Ni). This is also reflected by the compressibility (which was the subject of this investigation) and the thermal expansion.

(b) Among the Mn compounds investigated there are representatives with very large compressibilities $1/K_0$ (e.g. YMn_2).

(c) The thermal expansions of these compounds are intimately connected with the compressibility (the larger the compressibility the larger the thermal expansion).

In order to study whether the contribution of the spin fluctuations (which are known to exist in all of the Mn-based compounds, but which are especially prominent in YMn_2) is responsible for the unusual behaviour of the Y–Mn compounds, a comparison with the classical spin-fluctuation system UAl_2 has been carried out. The linear thermal expansion coefficient α of

UAl_2 ($(15.0 \pm 0.5) \times 10^{-6}$ K^{-1} at 300 K, determined within the present study) as well as the pressure dependence of the unit-cell volume of UAl_2 with $K_0 = 84$ GPa and $K_0' = 8.1$ [24] is typical for an intermetallic compound; i.e. the huge thermal expansion and compressibility of YMn_2 can hardly be attributed to the existence of spin fluctuations, at least in the sense of classical spin fluctuations as described by Moriya in [25].

There is however another mechanism which has been discussed in a previous paper which deals with the thermal expansion of Mn-based compounds [3]. Within the scope of the model presented there, it is assumed that there is a coexistence of two different types of Mn ions with different 3d-electronic configurations (denoted as N_h and N_l) in the paramagnetic state and that the two configurations differ as regards their ionic volumes. Furthermore, the assumption has been made that the concentration ratio N_h/N_l changes with temperature, thus causing an additional contribution to the thermal expansion. Since the thermal expansion and the compressibility are closely connected with each other, we now extend this model by assuming that the N_h/N_l ratio also changes with pressure. Applying this model to the three Y–Mn compounds, we have to take into account that the character of the temperature and pressure variation of the N_h/N_l ratio depends on the local Mn surrounding, leading to different values of the compressibility and the thermal expansion. The difference of the compressibility between the C15 compound YMn_2 on the one hand and YMn_{12} and Y_6Mn_{23} on the other hand might be attributed to there being several crystallographic sites in the latter compounds.

Acknowledgments

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