The magnetic phase diagram of $Tb_xY_{1-x}Mn_2$ intermetallics under pressure using neutron diffraction

1996 J. Phys.: Condens. Matter 8 8385

(http://iopscience.iop.org/0953-8984/8/43/029)

J. Phys.: Condens. Matter **8** (1996) 8385–8396. Printed in the UK

The magnetic phase diagram of $Tb_xY_{1-x}Mn_2$ intermetallics under pressure using neutron diffraction

J M De Teresa†, C Ritter‡, M R Ibarra†, Z Arnold§, C Marquina† and A del Moral†

† Departamento de Física de la Materia Condensada and Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza–CSIC, 50009 Zaragoza, Spain
‡ Institut Laue–Langevin, 38042 Grenoble Cédex, France
§ Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 00 Praha 6, Czech Republic

Received 17 April 1996, in final form 29 July 1996

Abstract. The magnetic phase diagram of the intermetallic compounds $Tb_xY_{1-x}Mn_2$ has been studied under pressure using neutron diffraction. At ambient pressure all compounds undergo a first-order magnetic transition as the Mn magnetic moment becomes local, giving rise to a transformed phase, with higher volume. Part of the sample can remain non-transformed and the two phases coexist below the transition temperature. As pressure is applied the relative volume percentages of the transformed phase and non-transformed phases change as the transformed phase becomes unstable under pressure. At high enough pressures only the non-transformed phase is present. Within the non-transformed phase, for $x > 0.2$ there is a transition to a magnetic structure which is reminiscent of the $DyMn_2$-like structure while for $x \leqslant 0.2$ the structure remains paramagnetic. In the transformed phase the $TbMn_2$-like magnetic structure develops at high Tb concentrations while at low Tb concentrations two different antiferromagnetic structures are visible, a YMn_2-like structure and a new antiferromagnetic structure unknown up to now. Across the intermediate-concentration range a magnetic ground state with short-range correlations is present.

1. Introduction

There are many magnetic systems which show volume changes associated with a first-order magnetic phase transition in which the magnitude of the magnetic moment changes. This behaviour appears in apparently very different systems such as FeRh [1] (where the antiferro–ferromagnetic transition is accompanied by stabilization of the Rh magnetic moment), $CeNi_{1-x}Co_xSn$ [2] (with a first-order Ce valence change), and the spin-fluctuating compounds AMn_2 (A = Tb, Sm, Y, Gd, Nd, Pr) (with sudden stabilization of magnetic moment at the Mn sites at low temperatures). In all these systems there is a strong relationship between magnetism and lattice which brings about large instabilities by applying an external magnetic field or presssure [1–4]. Much effort has been devoted to the study of the RMn_2 compounds (R = rare earth) due to the wide range of phenomena one finds in them (for a review see for instance [5]). In this paper we study the series $Tb_xY_{1-x}Mn_2$ by using neutron diffraction under pressure in order to depict its magnetic phase diagram under pressures ranging from 1 bar to 5 kbar.

The rich phenomenology found in the series $Dy_xY_{1-x}Mn_2$ [6] encouraged us to carry out this study. YMn_2 is a compound which shows strong spin fluctuations above T_N,

0953-8984/96/438385+12$19.50

the temperature at which it becomes antiferromagnetic. At T_N ($\approx$70–100 K) there is a first-order volume change associated with the appearance of a local moment at the Mn sites. The $2.8\mu_B$ Mn magnetic moments order in an antiferromagnetic helix [7, 8] (this structure will be called AF1 hereafter). In $DyMn_2$ the spin-canted structure of the Dy, with ferromagnetic and antiferromagnetic components, gives rise to the appearance of induced magnetic moment ($\approx 1.4\mu_B$) in one quarter of the Mn atoms [9]. The ordering of the Dy sublattice takes place at $\approx$40 K with antiferromagnetic ordering of the magnetic Mn atoms (this structure will be called F hereafter). No volume change associated with this transition can be seen [9] . Across the series $Dy_xY_{1-x}Mn_2$ one finds new magnetic structures arising from the competition of all the magnetic interactions. Unlike $DyMn_2$, $TbMn_2$ shows the first-order volume change when the Mn acquires a local moment at $T_N \approx 45$ K. The Tb and Mn magnetic moments are arranged in an antiferromagnetic structure [10] (called AF2 hereafter). Consequently, new magnetic states can also be expected across the series $Tb_xY_{1-x}Mn_2$.

Due to the strong magnetic instabilities the effect of applying magnetic field or pressure is expected to be large. Thus, in YMn_2 and $TbMn_2$ an applied pressure of 3 kbar avoids the appearance of magnetic moment at the Mn sites [11]. At intermediate pressures there is coexistence of two phases: a transformed phase with local magnetic moment at the Mn sites and a non-transformed phase with itinerant Mn moments. The transformed phase is unstable under an external magnetic field in $TbMn_2$ while it is stable in YMn_2 [3].

In a previous paper [12] we proposed preliminary magnetic phase diagrams for the transformed and non-transformed phases of the $Tb_xY_{1-x}Mn_2$ compounds based on macroscopic measurements (linear thermal expansion, AC susceptibility under pressure up to 7 kbar, and magnetostriction up to 14 T). The neutron diffraction provides an excellent tool to identify the magnetic structures of both phases as well as the relative percentage of the transformed phase and non-transformed phases at each pressure.

The linear thermal expansion measurements showed that at ambient pressure all the $Tb_xY_{1-x}Mn_2$ compounds undergo a first-order volume contraction (at $\approx$40 K for $x \geqslant 0.2$) ranging from $\approx$1.5% for $x = 1$ to $\approx$5% for $x = 0$, which is a hallmark of the existence of the transformed phase. Measurements of AC susceptibility under pressure indicated that the transformed phase is unstable under pressure for all the compounds. The peaks in the AC susceptibility which appear in the Tb-rich compounds ($x \geqslant 0.6$) under pressure were associated with para–ferrimagnetic transitions within the non-transformed phase. Magnetostriction measurements allowed us to establish that for the Tb-rich compounds ($x \geqslant 0.6$) the magnetic structure is unstable under applied magnetic field, which suggested the AF2-like structure. For the Y-rich compounds ($x \leqslant 0.2$) the magnetic structure is stable under applied magnetic field, which suggested the AF1-like structure. The existence of magnetic order in the compounds around the concentration $x = 0.4$ was impossible to determine with our macroscopic measurements.

In order to investigate the magnetic ground-state structures of the transformed and non-transformed phases across the whole $Tb_xY_{1-x}Mn_2$ series, and how the non-transformed phase becomes stabilized under pressure, we have carried out neutron diffraction experiments under pressures up to 5 kbar.

2. Experiments

The polycrystalline compounds $Tb_xY_{1-x}Mn_2$ (with $x = 0.2$, 0.4, 0.6, and 0.8) were prepared by arc melting the high-purity constituents, R (99.9%), and Mn (99.99%). 3% rare earth element was added over the nominal concentration in order to avoid the formation of the secondary phase R_6Mn_{23}. The samples were melted several times and subsequently annealed for 5 d at 800 °C under a stabilized Ar atmosphere. The presence of the C15 cubic Laves phase was confirmed by x-ray and neutron powder diffraction. A small quantity of the secondary phase R_6Mn_{23} was detected for the compounds $x = 0.2$, 0.4, and 0.6.

The neutron diffraction experiments were performed using the D1B high-intensity powder diffractometer at the Institut Laue–Langevin (ILL), Grenoble. D1B uses a 2.52 Å monochromatic neutron beam and has a 400-element linear multidetector covering an angular range of 80 °. The multidetector allows rapid data collection, typical diffraction patterns being accumulated in 10 min intervals. For the zero-pressure experiments the powdered samples were contained in a vanadium can mounted in a standard 'orange' cryostat. This gas cell works in connection with a gas pressure generator. A 3 kbar two-stage membrane compressor delivers He to an oil driver intensifier. The later is connected to the pressure cell via a flexible capillary. The pressure is measured with high precision in a special manometer cell connected in parallel. The pressure can be changed *in situ* and at the desired sample temperature, as long as this is not below the freezing point of He. It was not possible to perform an accurate refinement of the neutron diffraction spectra under pressure because of the high background introduced by the presure cell, which produced a large incoherent scattering contribution and the presence of extra peaks.

AC susceptibility measurements on $Tb_{0.2}Y_{0.8}Mn_2$ were carried out with a commercial SQUID magnetometer using a maximum applied field of 1 Oe and frequency of 20 Hz.

3. Results and discussion

3.1. The high-Tb-content region ($x = 0.8$ and 0.6)

The $x = 0.8$ and $x = 0.6$ compounds behave in a similar way. We report here the results which correspond to the $x = 0.8$ compound. The same conclusions apply for the $x = 0.6$ compound.

3.1.1. $P = 1$ bar. In figure 1 the neutron diffraction thermogram of $Tb_{0.8}Y_{0.2}Mn_2$ without external pressure is shown. Below $T_N = 52$ K a set of magnetic peaks appear. They were also reported by Ballou *et al* [13] in a previous paper on $Tb_xY_{1-x}Mn_2$ at ambient pressure. They correspond to the magnetic structure of $TbMn_2$ [10] (AF2), characterized by a propagation vector $[\tau_x, \tau_y, 0]$ with $\tau_x = \tau_y = \frac{2}{3}$. In fact our fits indicate that for the $x = 0.8$ compound $\tau_x = 0.779$ and $\tau_y = 0.620$, and for the $x = 0.6$ compound $\tau_x = 0.84$ and $\tau_y = 0.58$. In agreement with the linear thermal expansion results [12], we have obtained from the shifting of the nuclear peaks at T_N a volume change of ≈1.6% for both compounds. This volume change is connected with the appearance of magnetic moments at the Mn sites as we have pointed out in section 1. From our fits the following magnetic moments are found: for $x = 0.8$, $\mu_{Tb\,site} = 4.9\mu_B$ and $\mu_{Mn\,site} = 1.2\mu_B$; for $x = 0.6$, $\mu_{Tb\,site} = 4.1\mu_B$ and $\mu_{Mn\,site} = 1.2\mu_B$. No sign of non-transformed phase is seen for either sample at ambient pressure.

3.1.2. High pressure. In $TbMn_2$ it was shown [11] that under pressures greater than 2 kbar the low-temperature magnetic structure is $DyMn_2$-like (F). The F structure is a canted magnetic structure in which only one in four Mn atoms (those in a strongly magnetically polarized environment) carry a magnetic moment. In figure 2 the neutron diffraction thermogram of $Tb_{0.8}Y_{0.2}Mn_2$ under 3 kbar is shown. The magnetic peaks which correspond to the F structure can be seen below $T \approx 53$ K. At around $T \approx 25$ K a small decrease

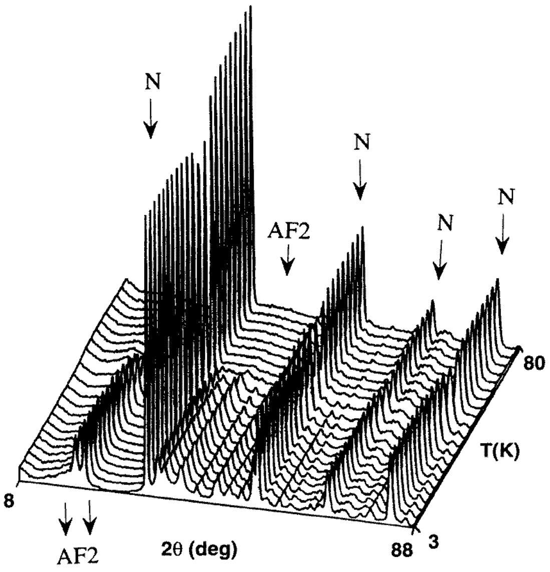

Figure 1. The neutron diffraction thermogram of $Tb_{0.8}Y_{0.2}Mn_2$ at 1 bar. The arrows indicate the origins of the peaks (N, nuclear; AF2, see the text).

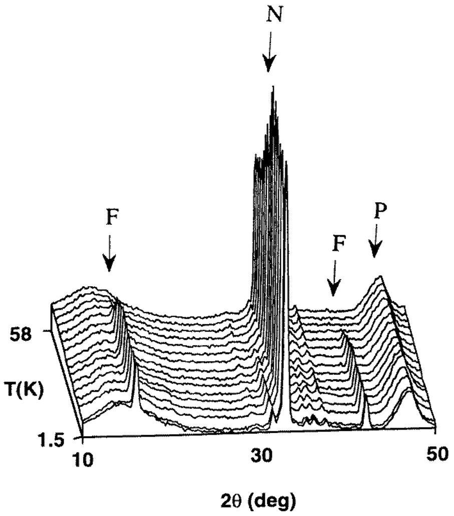

Figure 2. The neutron diffraction thermogram of $Tb_{0.8}Y_{0.2}Mn_2$ at 3 kbar. The arrows indicate the origin of the peaks (N, nuclear; P, pressure cell; F, see the text).

in the magnetic peak intensity exists. This takes place because a small part of the sample still transforms into the transformed phase. From the fits of the intensity of the peaks we can say that the volume change is less than 0.5%. This value could not be accurately determined as the solidification of helium in the pressure cell leads to a volume effect which screens the effect from the sample. At 1.5 K the amount of transformed phase is about 7%.

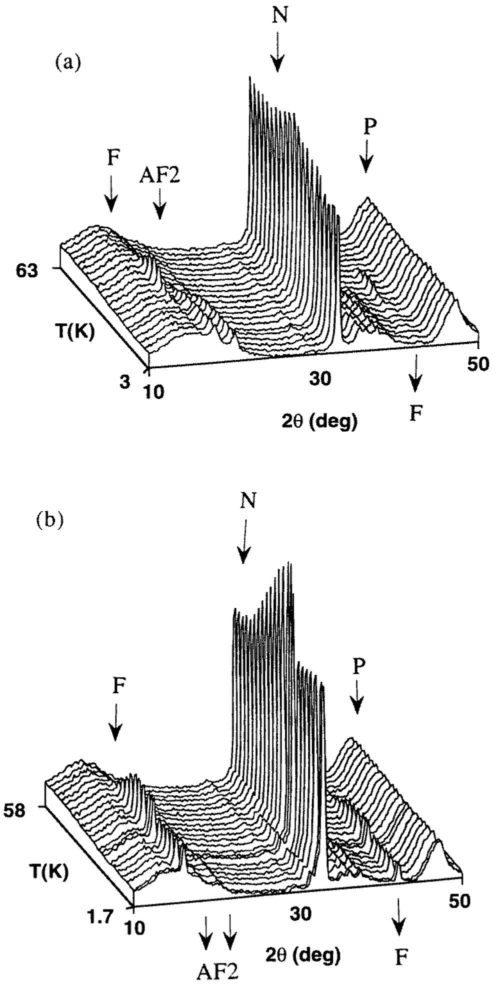

Figure 3. The neutron diffraction thermograms of $Tb_{0.8}Y_{0.2}Mn_2$ at (a) 1.4 kbar and (b) 2.2 kbar. The arrows indicate the origin of the peaks (N, nuclear; P, pressure cell, AF2 and F, see the text).

With pressure values slightly larger than 3 kbar only the non-transformed phase must be present. For $Tb_{0.6}Y_{0.4}Mn_2$ the behaviour is similar. At $P = 3$ kbar the F structure appears at $T \approx 42$ K and the small presence of transformed phase is visible below $T_N \approx 29$ K. At $T = 2$ K there is about 38% transformed phase. At 4 kbar only the non-transformed phase is present across the whole range of temperatures ($T \geqslant 1.5$ K).

3.1.3. Intermediate pressure. In figure 3(a) and (b) the thermograms of $Tb_{0.8}Y_{0.2}Mn_2$ at 1.4 and 2.2 kbar respectively are shown. For both pressures the magnetic peaks which correspond to the F structure appear at around 50 K. At 1.4 kbar the transformed phase, with the AF2 structure, appears at around 37 K. The peaks from the non-transformed phase

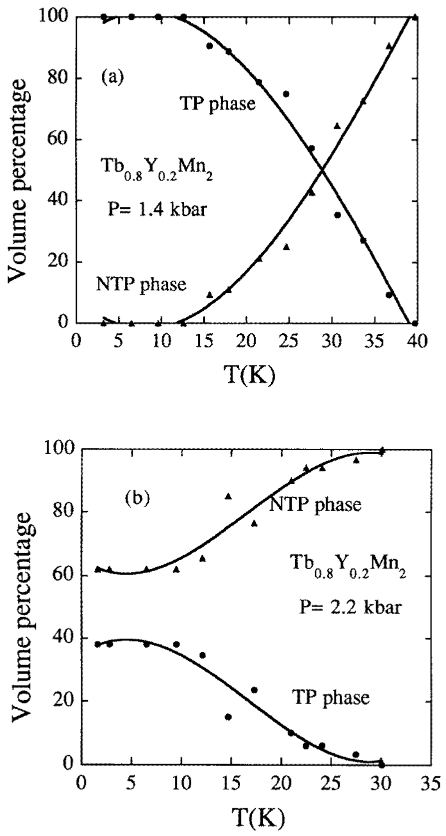

Figure 4. The volume percentages of the transformed (TP) and non-transformed (NTP) phases (see text) of $Tb_{0.8}Y_{0.2}Mn_2$ as a function of temperature at (a) 1.4 kbar and (b) 2.2 kbar.

weaken below this temperature to disappear at the lowest temperatures. In figure 4(a) the volume percentages of the transformed and non-transformed phases at 1.4 kbar as a function of temperature are shown. At 2.2 kbar the transformed phase appears at around 25 K, decreasing the intensity of the NTP-phase peaks. However the sample is not completely transformed at the lowest temperature. In figure 4(b) the volume percentages of both phases at 2.2 kbar are shown. At 1.7 K there is around 40% transformed and 60% non-transformed phases. From our fits we have obtained that the propagation vector changes with pressure. In $Tb_{0.8}Y_{0.2}Mn_2$, for $P = 1.4$ kbar we obtained $\tau_x = 0.712$ and $\tau_y = 0.647$, and for $P = 2.2$ kbar, $\tau_x \approx 0.68$ and $\tau_y \approx 0.66$. Consequently, applying external pressure brings about a shifting of the propagation vector towards the value found in pure $TbMn_2$ ($\tau_x = \tau_y = 0.666$). For $x = 0.8$ and 1.4 kbar the fits gave $\mu_{Tb site} = 4.2\mu_B$ and $\mu_{Mn site} = 1.2\mu_B$.

3.2. The high-Y-content region ($x = 0.2$)

3.2.1. $P = 1$ bar. In figure 5 the neutron diffraction thermogram of $Tb_{0.2}Y_{0.8}Mn_2$ at 1 bar is shown. The magnetic peaks which correspond to the YMn_2-like (AF1) structure can be seen below $T_N = 57$ K. However at $T \approx 40$ K these peaks decrease and new antiferromagnetic peaks appear at $2\Theta = 34.7$ and 44° ($d = 4.23$ and 3.37 Å). A detailed study of

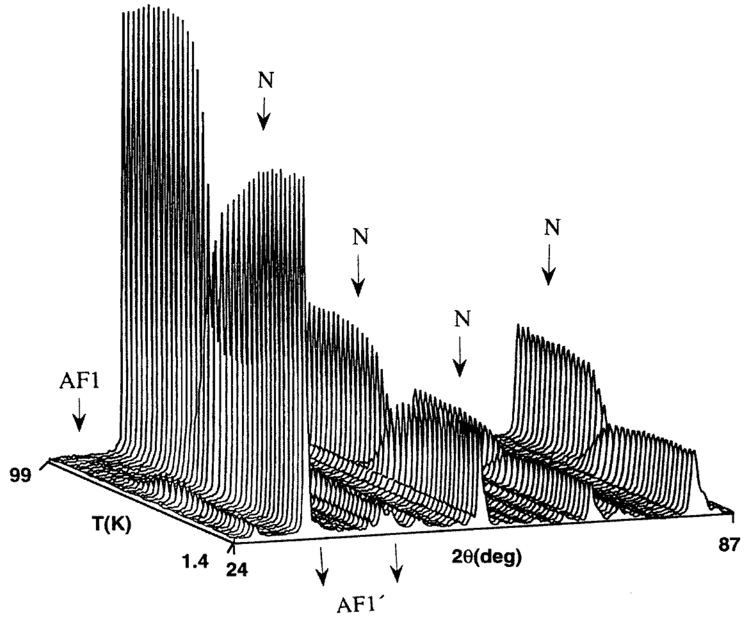

Figure 5. The neutron diffraction thermogram of $Tb_{0.2}Y_{0.8}Mn_2$ at 1 bar. The arrows indicate the origin of the peaks (N, nuclear; AF1 and AF1′, see the text).

the neutron pattern at low temperature showed that a new magnetic phase is present (called AF1′ hereafter). This structure seems to be also present in $Dy_{0.2}Y_{0.8}Mn_2$ [6] but scarce information has been produced about this structure. In figure 6(a) the refined lattice constant as a function of temperature is shown. At T_N a sharp increase in the lattice parameter is seen but at $T \approx 40$ K a decrease is observed. This can be connected to the appearance of the new magnetic phase. We have also performed AC susceptibility measurements with a SQUID magnetometer in order to detect any significant change in the magnetic structure. In figure 6(b) the real part (χ') of the AC susceptibility is shown as a function of temperature. A change of slope is visible at $T \approx 40$ K, which is in agreement with the appearance of the AF1′ magnetic structure. The χ' values are reasonable for antiferromagnetic ordering. All this makes us think that a new antiferromagnetic ground state develops in $Tb_{0.2}Y_{0.8}Mn_2$ at low temperature. The exact magnetic structure is not yet known; it seems, however, closely connected to the YMn_2-like structure as the AF1-like magnetic peaks persist. Further high-resolution experiments are necessary to solve this problem.

3.2.2. High pressure. In figure 7 the thermogram of $Tb_{0.2}Y_{0.8}Mn_2$ at $P = 3$ kbar is shown. The sample remains as non-transformed phase across the whole range of temperatures studied ($T \geqslant 1.7$ K). No magnetic transition was detected within the non-transformed phase as the low Tb content prevents the long-range magnetic order of the rare earth sublattice.

3.3. The region around $x = 0.4$

The macroscopic measurements (AC susceptibility and magnetostriction [12]) were unable to elucidate the magnetic structures of the transformed and non-transformed phases of $Tb_{0.4}Y_{0.6}Mn_2$. The neutron diffraction measurements have allowed us to discover them.

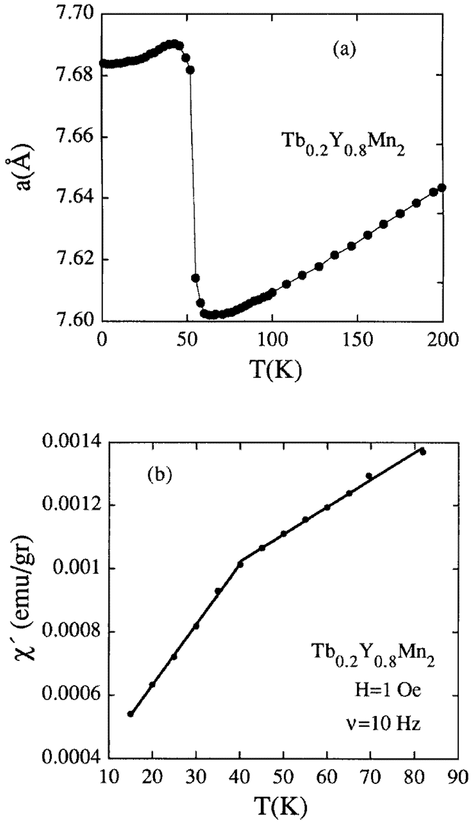

Figure 6. (a) The refined lattice parameter as a function of temperature of $Tb_{0.2}Y_{0.8}Mn_2$ at 1 bar. (b) The real part (χ') of the AC susceptibility of $Tb_{0.2}Y_{0.8}Mn_2$ at frequency 20 Hz and maximum applied field 1 Oe.

3.3.1. $P = 1$ bar. From the thermogram of $Tb_{0.4}Y_{0.6}Mn_2$ at 1 bar we obtained that at $T_N = 42$ K the sample starts to transform and at low temperatures all the sample is in the transformed phase. The volume change is 1.5%. As there is no clear magnetic peak in the neutron spectra at low temperatures, we have plotted (see figure 8) the difference between the spectra at low ($\approx$1.5 K) and high temperatures ($\approx$50 K). This kind of plot allows us to check whether any magnetic correlation exists at low temperatures. One can see in figure 8 that there is a clear AF2-like magnetic correlation (additional neutron scattering contribution over the background at the position of the AF2 peaks). Therefore one must conclude that for $Tb_{0.4}Y_{0.6}Mn_2$ there is short-range AF2-like magnetic order (SRO) in the transformed phase.

3.3.2. High pressure. As pressure is applied the transformed phase becomes unstable but at 1 and 2 kbar the magnetic peaks in the non-transformed phase are not clearly visible, probably due to the low percentage of non-transformed phase. However at 3 kbar (with $\approx$60% non-transformed phase) and 5 kbar (with 100% non-transformed phase) the magnetic

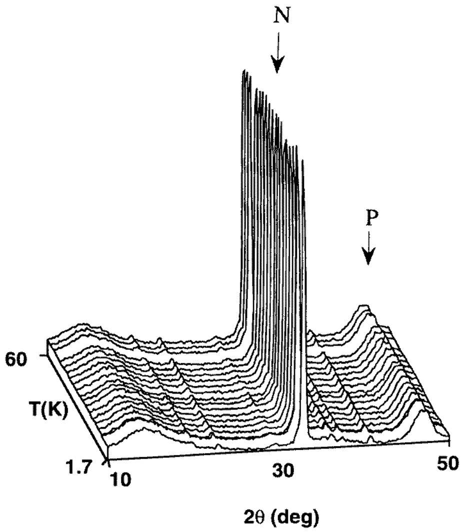

Figure 7. The neutron diffraction thermogram of $Tb_{0.2}Y_{0.8}Mn_2$ at 3 kbar. The arrows indicate the origin of the peaks (N, nuclear; P, pressure cell).

peaks which correspond to the F structure can be clearly seen. In figure 9 the thermogram of $Tb_{0.4}Y_{0.6}Mn_2$ at $P = 5$ kbar is shown. Below $T_C \approx 32$ K the magnetic peaks corresponding to the F magnetic structure can be seen.

3.4. Discussion

In $Tb_xY_{1-x}Mn_2$ there are two magnetic states at low temperatures very close in energy (associated with the transformed and non-transformed phases) but of very different unit cell volume and magnetic structure. One finds coexistence of these two different phases under certain conditions. At ambient pressure the transformed phase, with local Mn magnetic moment and high volume, is the phase of minimum energy. At high pressures the non-transformed phase, with itinerant Mn moments and low volume, is the phase of minimum energy. At intermediate pressures the general situation is the coexistence of both phases. Within each phase different magnetic structures can occur depending on the Tb content.

4. Magnetic phase diagrams

In figure 10(a) we show the magnetic phase diagram of the transformed phase according to the neutron diffraction measurements. At ambient pressure for all the compounds there is a first-order phase transition when the Mn magnetic moment becomes local. The transition temperature depends on the Y content, being around 50 K for $x \geqslant 0.2$ and 90 K for $x = 0$. In the compounds with high Y content the Mn magnetic moments order antiferromagnetically with the AF1 (YMn_2-like) structure or the unknown AF1′ structure. For $x = 0.4$ the absence of magnetic peaks and the presence of magnetic correlations point to short-range magnetic ordering. Such correlations appear at the positions where the magnetic peaks of the AF2 ($TbMn_2$-like) structure appear. In the high-Tb-content region the Mn magnetic moments order with the AF2 structure. When pressure is applied the transformed phase appears at

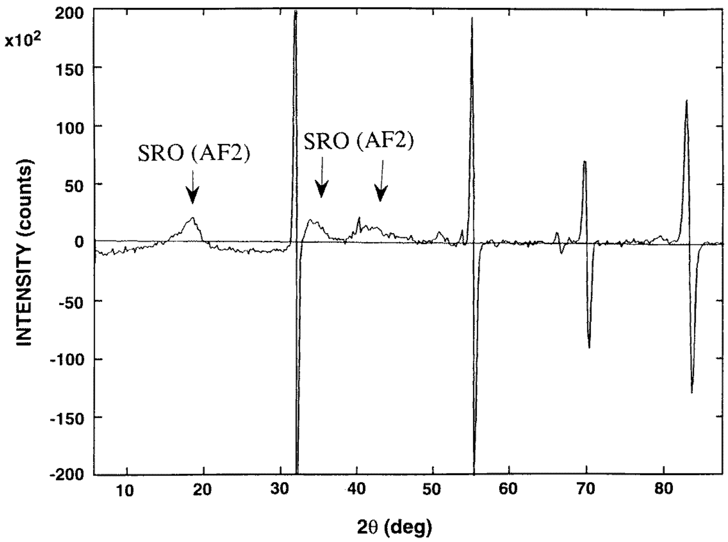

Figure 8. The difference between the neutron scattering intensities at low (1.5 K) and high (50 K) temperatures of $Tb_{0.4}Y_{0.6}Mn_2$ at 1 bar. The arrows indicate the SRO contribution (see the text).

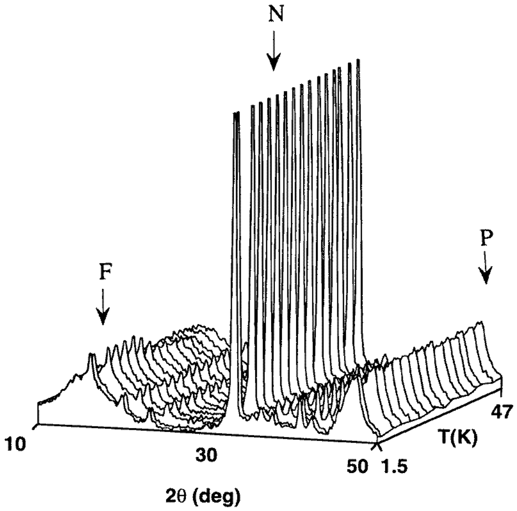

Figure 9. The neutron diffraction thermogram of $Tb_{0.4}Y_{0.6}Mn_2$ at 5 kbar. The arrows indicate the origin of the peaks (N, nuclear; P, pressure cell, AF2, see the text).

lower temperatures (see in figure 10(a) that at 3 kbar the transformed phase has completely disappeared for $x \leqslant 0.2$), keeping however the same magnetic structure. In figure 10(b) we show the magnetic phase diagram of the non-transformed phase. The values of T_C have been obtained from the AC susceptibility measurements [12] as this information was less accurate when obtained with our neutron results. Two facts are relevant. First, only two magnetic states are possible at low temperatures. For high Tb content the F ($DyMn_2$-

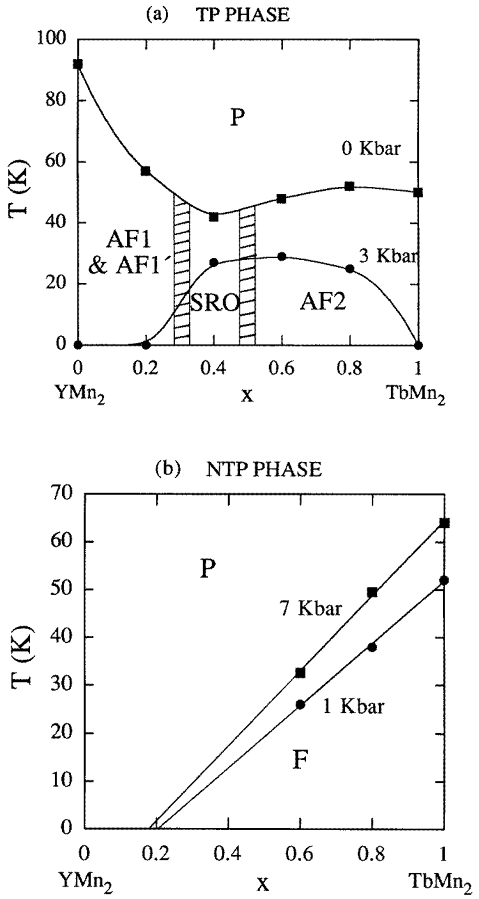

Figure 10. Magnetic phase diagrams of $Tb_xY_{1-x}Mn_2$: (a) transformed phase (TP) at 1 bar and 3 kbar according to the neutron diffraction results; (b) non-transformed phase (NTP) at 1 and 7 kbar according to the AC susceptibility results. Lines are visual guides.

like) structure occurs and for high Y content the sample remains paramagnetic. Second, as pressure increases T_C increases. This fact is due to the reinforcement of the Tb–Tb exchange interaction with pressure. In our previous paper [12] we suggested the possibility of the loss of the long-range magnetic order in the non-transformed phase for the compounds with high enough Y concentration. The neutron results indicate that the magnetic peak width does not change with the Y content, which would be a hallmark of short-range or spin-glass magnetic behaviour. The situation can be close to a crossover from long-range to short-range order but this is not still manifested as a broadening of the neutron diffraction magnetic peaks.

5. Conclusions

All the experimental results in the series of intermetallic compounds $Tb_xY_{1-x}Mn_2$ under pressure and magnetic field can only be explained considering the existence of two phases whose magnetic phase diagrams are confirmed by the present experiments of neutron diffraction under pressure. At ambient pressure and low temperatures the Mn magnetic moment becomes local, giving rise to a transformed phase with a strong lattice expansion. The magnetic structure in this transformed phase is YMn_2-like (or the new unknown AF1′ structure) for the high-Y-content region, $TbMn_2$-like for the high-Tb-content region, and short-range magnetic order of the $TbMn_2$-like structure for compounds around $x = 0.4$. When pressure is applied there is coexistence of the transformed phase and a non-transformed phase. At high pressure only the non-transformed phase exists. The non-transformed phase orders with the $DyMn_2$-like structure for high Tb content and remains paramagnetic for low Y content.

Acknowledgments

We are grateful to Conrado Rillo for help in the SQUID measurements and the Spanish CICYT for financial support.

References

[1] Ibarra M R and Algarabel P A 1994 *Phys. Rev.* B **50** 4196

[2] Adroja D T, Rainford B D, De Teresa J M, del Moral A, Ibarra M R and Knight K S 1995 *Phys. Rev.* B **52** 12 790

[3] Ibarra M R, Marquina C, Algarabel P A, De Teresa J M, Ritter C and del Moral A 1994 *Proc. 13th Int. Workshop on Rare Earth Magnets and their Applications (Birmingham 1994)* ed C A F Manwaring *et al* p 127

[4] Hauser R, Bauer E, Gratz E, Häufler Th, Hilscher G and Wiesinger G 1994 *Phys. Rev.* B **50** 13 493

[5] Shiga M 1988 *Physica* B **149** 293

[6] Ritter C, Cywinski R, Kilcoyne S H, Mondal S and Rainford B D 1994 *Phys. Rev.* B **50** 9894

[7] Cywinski R, Kilcoyne S H and Scott C A 1991 *J. Phys.: Condens. Matter* **3** 6473

[8] Deportes J, Ouladdiaf B and Ziebeck K R A 1987 *J. Physique* **48** 1029; 1987 *J. Magn. Magn. Mater.* **70** 129

[9] Ritter C, Cywinski R, Kilcoyne S H 1991 *J. Phys.: Condens. Matter* **3** 727

[10] Corliss L M and Hastings J M 1964 *J. Appl. Phys.* **35** 1051
Brown P J, Ouladdiaf B, Ballou R, Deportes J and Markosyan A S 1992 *J. Phys.: Condens. Matter* **4** 1103

[11] Mondal S, Cywinski R, Kilcoyne S H, Rainford B D and Ritter C 1992 *Physica* B **180&181** 108

[12] De Teresa J M, Ibarra M R, Ritter C, Marquina C, Arnold Z and del Moral A 1995 *J. Phys.: Condens. Matter* **7** 5643

[13] Ballou R, Deportes J, Lemaire R, Rouault P and Soubeyroux L L 1990 *J. Magn. Magn. Mater.* **90&91** 559