Journal of Alloys and Compounds 404–406 (2005) 160–162

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Valence band and magnetic moment of Mn in $TbMn_2$ and $TbMn_2D_2$ studied by $K_{\beta5}$ emission X-ray spectroscopy

E. Jarocki*, A. Kozłowski, H. Figiel

Solid State Physics Department, Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland

Received 16 August 2004; received in revised form 4 November 2004; accepted 9 November 2004

Abstract

Manganese $K_{\beta5}$ X-ray fluorescence spectra were measured for Mn-metal, $TbMn_2$ and $TbMn_2D_2$. Experimental results show that in both examined Tb-Mn compounds intensities of $K_{\beta5}$ lines are greatly reduced approximately to one third of those in elemental Mn. Since the $K_{\beta5}$ line is usually believed to be due to electron quadrupole transition from Mn 3d to the $1s^{-1}$ hole, then the observed shape of this line can probe the d-states of manganese. The results are compared to the relevant studies of $K_{\beta1,3}$ lineshape and the neutron diffraction investigations. We suggest that the manganese magnetic moment in both compounds is frustrated or in a noncollinear arrangement.

Keywords: X-ray spectroscopy; Hydrogen storage materials; Magnetically ordered materials; Electronic band structure

1. Introduction

Studies on the X-ray emission K_β line satellites in transition metals and their compounds may help to understand the electronic structure of transition metal compounds and their magnetic states. The rare earth-transition-metal compounds and their hydrides are subject of a great interest due to their structural and magnetic properties, and also due to their possible technical applications. In this paper we analyze $K_{\beta5}$ line emission profile of manganese in $TbMn_2$ and $TbMn_2D_2$ compounds. Both investigated compounds have magnetic and crystallographic structures determined by neutron techniques [1–4], but the details of magnetic moment values and their arrangement are still not clear. For example, different magnetic structures for $TbMn_2$ and $TbMn_2D_2$ were found. Also, some peculiarities of magnetic moments were reported in both compounds. In particular, the manganese magnetic moments in the deuterated sample split into two values, $Mn_1 = 3.3\mu_B$ and $Mn_{2,3,4} = 1.23\mu_B$, as found in [4]. These values were determined under an assumption of collinear magnetic structures with reasonably good magnetic reliability factor. However, it is not clear if the low moments on $Mn_{2,3,4}$ sites are real values or are spurious effects of frustration or uncollinear arrangement, as was suggested in [2,3] for $TbMn_2$.

To further study this problem, we have measured the line shape of the $K_{\beta5}$ line, since it is usually interpreted as the quadrupolar 3d to 1s transition, i.e. could be relevant to the manganese d-band [5–8].

2. Experimental details

The intermetallic compound $TbMn_2$ was prepared from high purity materials (99.99% for Tb and 99.9% for Mn) by induction melting technique in Ar inert gas under atmospheric pressure. For better homogeneity samples were remelted several times under Ar flow and then checked for proper structure by X-ray diffraction. The deuteration to $TbMn_2D_2$ was carried out with the use of standard technology [9]: the powdered sample (grain diameter was below

---

* Corresponding author. Tel.: +48 12 617 2904; fax: +48 12 634 1247.
E-mail address: ejarocki@uci.agh.edu.pl (E. Jarocki).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2004.11.115

40 μm) was first kept several hours in the reactor evacuated below 10^{-8} Pa and at temperature 600 K. During the deuteration the temperature of 300 K was maintained. The deuterium content was estimated from the reduction of the gas pressure with the possible uncertainty of 5%. After the deuteration the sample was annealed for 48 h at 450–500 K. After the final stage of deuteration the materials were again analyzed by X-ray diffraction. The detection of the K_{β} lines was realized by the TUR M62 X-ray apparatus with the specially adapted horizontal goniometer HZG-3. To excite the samples, Cu Kα radiation was used at 35 kV and 25 mA. The spectrum around Kβ line was analyzed by the (4 0 0) reflection of a LiF crystal and detected by a proportional counter. The scanning was performed with the step of 0.02° in theta with the limits including both $K_{\beta 1,3}$ and $K_{\beta 5}$ line profiles. The measuring time for each energy point was 100 min. To compensate for possible statistical errors in diffraction pattern each sample was measured several times. The sample of pure manganese was also measured as a standard for angle fine correction and, as an important material, for comparison.

3. Results and discussion

The X-ray $K_{\beta 5}$ profile for elemental Mn, $TbMn_2$ and $TbMn_2D_2$ are shown in Fig. 1. The intensity data were normalized to $K_{\beta 1,3}$ peak to enable their comparison. Also, the corrections due to $K_{\beta 1,3}$ tail on the left side of Mn $K_{\beta 5}$ profiles were introduced.

The main feature of the patterns for $TbMn_2$ and $TbMn_2D_2$ is the much lower integral intensity of $K_{\beta 5}$ line in comparison to that for elemental manganese. The second feature, less apparent due to poor statistics, is that the structure of $K_{\beta 5}$ line reveals two weak maxima with about 5–7 eV distance between them. The ratio of $K_{\beta 5}$ integral intensities for both intermetallic compounds versus that for Mn metal is about 0.4.

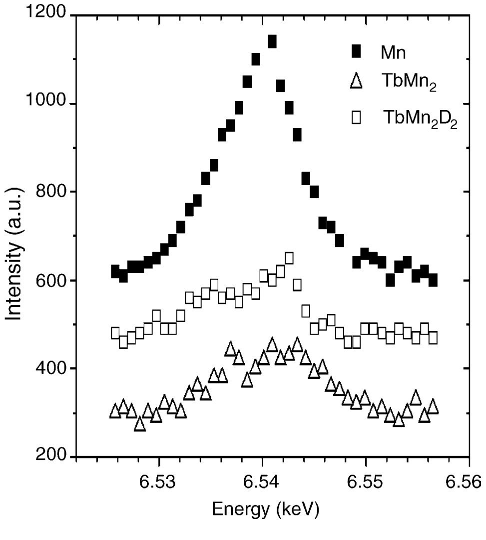

Fig. 1. $K\beta_5$ line profiles for $TbMn_2$ and $TbMn_2D_2$, and for Mn metal for comparison.

Assuming that the $K_{\beta 5}$ peak is due to the quadrupole transition s–d, as usually interpreted in the literature, and that its intensity is roughly proportional to the number of d-like electrons, one can conclude that the number of these electrons is much higher in pure manganese than in both investigated compounds. The elemental manganese d-band is strongly hybridized with s and p electrons [10,11], so the body of $K_{\beta 5}$ peak derives at least from about seven electrons (this number results in low magnetic moment of manganese metal). Hence, lower $K_{\beta 5}$ intensities for $TbMn_2$ and $TbMn_2D_2$ mean that less d-like electrons participate in the transition. The number 0.4 of intensity ratios means that the manganese d-band in $TbMn_2$ and $TbMn_2D_2$ is less hybridized with s–p bands (i.e. d band is more isolated) as compared to pure manganese. This may be confirmed also by $K_{\beta 5}$ line profiles, where two broad maxima, reflecting probably e and t levels of the d band are visible.

Neutron diffraction data for $TbMn_2$ and $TbMn_2D_2$ [1–4] suggest rather complicated magnetic structures with frustrated magnetic Mn moments. Latest experiments on a deuterated sample [4] (this sample was also used in our measurements) gave two magnetic moments of manganese, $Mn_1 = 3.3\mu_B Mn_{2,3,4} = 1.2\mu_B$, in different crystallographic positions with a collinear structure assumed. The values for $Mn_{2,3,4}$ are then too low as compared to that expected from our experimental results from more isolated d-band electrons. It may indicate that $Mn_{2,3,4}$ moments posses higher values than determined from the neutron analysis, but that they are in the frustrated or noncollinear arrangement.

The presence of deuterium in $TbMn_2D_2$ stabilizes a magnetic structure different from that of $TbMn_2$, but apparently barely influences the d-band of manganese in the samples as one may conclude observing insignificant changes in $K_{\beta 5}$ shape between deuterated and pure material.

Additional information on the spin state of manganese in $TbMn_2$ and $TbMn_2D_2$, which agrees with our above conclusion, can be drawn from the analysis of $K_{\beta 1,3}$ low energy satellites. Using the same method of satellite position analysis as in our previous papers [12,13], we have obtained 2.7–2.9 magnetically uncompensated manganese electrons for $TbMn_2$ and $TbMn_2D_2$. Thus, Mn atoms are in rather high magnetic moment state in both samples, contrary to the value $1.2\mu_B$ obtained in [4] for particular manganese sites in $TbMn_2D_2$.

4. Conclusions

Experimental $K_{\beta 5}$ line profiles for $TbMn_2$ and $TbMn_2D_2$ have much lower intensities than for elemental manganese. The d-band in those compounds is thus less hybridized than in pure manganese and hence, the manganese magnetic moment has probably higher value than $1.2\mu_B$ [4]. Mn magnetic moment value of about $3\mu_B$ in our samples also results from $K_{\beta 1,3}$ low energy satellites positions. Both these findings contradict with neutron diffraction data interpretation in

[2–4], where lower manganese magnetic moments were inferred. Consequently, to explain this discrepancy, we suggest the existence of some frustrated or noncollinear manganese magnetic moment arrangement in these compounds.

Acknowledgments

This work was supported by KBN—State Committee for Scientific Research. The help from J. Sokulski is greatly acknowledged.

References

[1] L.M. Corlis, J.M. Hastings, J. Appl. Phys. 35 (1964) 1051–1053.
[2] R. Ballou, P.J. Brown, J. Deportes, A.S. Markosyan, B. Ouladdiaf, J. Magn. Magn. Mater. 104–107 (1992) 935–936.
[3] P.J. Brown, B. Ouladdiaf, R. Ballou, J. Deportes, A.S. Markosyan, J. Phys.: Condens. Matter 4 (1992) 1103–1113.
[4] A. Budziak, H. Figiel, J. Żukrowski, E. Gratz, B. Ouladdiaf, J. Phys.: Condens. Matter 13 (2001) L871–L877.
[5] S.D. Gamblin, D.S. Urch, J. Electron. Spectr. Rel. Phen. 113 (2001) 179–192.
[6] K. Sakurai, H. Eba, Nucl. Insr. Methods Phys. Res. B199 (2003) 391–395.
[7] Y. Watanabe, J.T. Okada, H. Shoji, S. Nanao, J. Alloys Compd. 342 (2002) 422–426.
[8] E.Z. Kurmayev, G.P. Shveikin, S.A. Nemnonov, Phys. Stat. Sol. (b) 60 (1973) K65–K68.
[9] H. Figiel, J. Przewożnik, V. Paul-Boncour, A. Lindbaum, E. Gratz, M. Latroche, M.H. Escorne, A. Percheron-Guegan, P. Mietniowski, J. Alloys Compd. 274 (1998) 29–37.
[10] E.O. Wollan, Phys Rev. 117 (1960) 387–401.
[11] P. Jounard, G. Giorgi, C. Bonnelle, Phys. Rev. A65 (2002) 032507-1-6.
[12] E. Jarocki, Phys. Stat. Sol. (b) 204 (1997) 857–861.
[13] E. Jarocki, L. Dargel-Sulir, A. Kozłowski, Phys. Stat. Sol. (b) 234 (2002) 654–659.