Materials Science-Poland, Vol. 25, No. 2, 2007

About negative magnetization in non-superconducting intermetallics

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The negative magnetization for ternary and pseudoternary compounds with the tetragonal $ThMn_{12}$ and rhombohedral Th_2Zn_{17} type structure is presented considering various magnetic ordering types. This phenomenon has been observed in compounds of rare earth and uranium. Comparing pecularities of the temperature dependence of the magnetization/magnetic susceptibility we try to find a common reason for this behaviour. The most attractive seems to be the difference in the anisotropy magnitude and direction of the individual magnetic sublattices as well as the crystallographic imperfections.

Key words: *rare-earth intermetallics; magnetic properties; negative magnetization*

1. Introduction

Recently, a few papers appeared describing the negative magnetization in $YbFe_4Al_8$ [1–3]. However, a similar behaviour has been presented for other compounds with the same $ThMn_{12}$ tetragonal type of structure with an f electron element being heavy rare earth [4] as well as the uranium [5] atoms. Also, one representative of the Th_2Zn_{17} rhombohedral type of structure, $Tb_{2.1}Co_{14.9}Si_3$, has been reported to exhibit a negative magnetization [6]. No convincing explanation of this behaviour has been proposed up to now. In the present paper, we review reported properties of the investigated compounds, establishing similarities and differences between them. We also provide preliminary results of magnetic investigations of imperfect single crystal of $YbFe_4Al_8$.

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2. Results and discussion

Let us inspect similarities between the discussed compounds. All of them are ternary or, more exactly, pseudoternary alloys. Moreover, it seems that at least in the compounds of the heavy rare earth one deals with two or more magnetic sublattices. Therefore, these compounds could be treated as ferrimagnetic ones. This statement is not so obvious in the case of alloys of U.

The earliest report concerns the alloys of magnetic heavy rare earths [4] and perhaps the authors were not very convinced about the physical reality of their observation because the results have never been published in regular journals. In Figure 1, magnetization versus temperature for $SmFe_5Al_7$ in a low field (30 Oe) is shown [4].

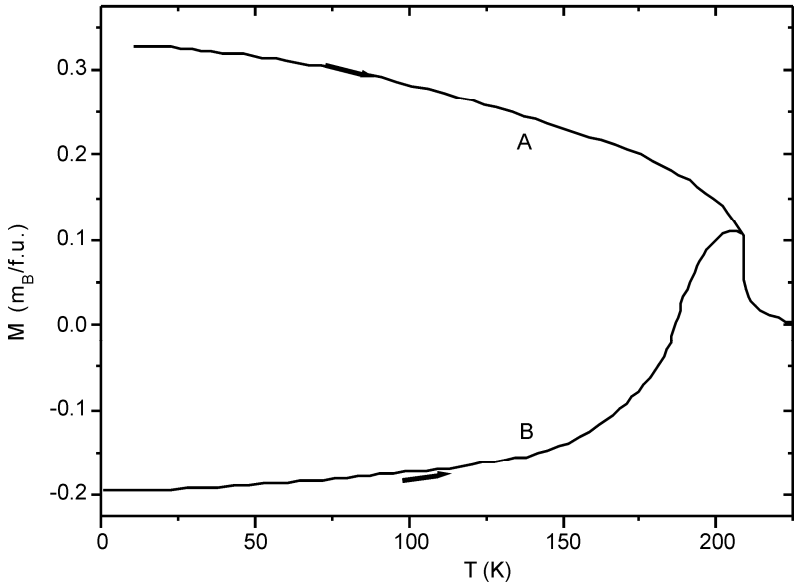

Fig. 1. Magnetization vs. temperature for $SmFe_5Al_7$ [4]

Curve A was obtained on increasing the temperature after slowly cooling the sample, whereas curve B was obtained after cooling the sample to 4.1 K within a few seconds. This pronounced difference between these two curves indicates a strong thermal hysteresis, different anisotropy in various magnetic sublattices and time dependent magnetization. In turn, an unusual behaviour of $TbFe_5Al_7$ and its derivative is presented in Fig. 2. Curve A was obtained when the sample was cooled in zero field, curve B was obtained when the sample was cooled in 100 Oe and then the measurement was carried out upon increasing temperature. Finally, curve C presents the results obtained on decreasing temperature. The quaternary alloy $TbFe_5Al_5Ge_2$ demonstrates different temperature dependence of magnetization with minimum and negative values between ca. 70 K and 120 K. The latter result is particularly peculiar

but at the same time strongly suggests that crystallographic disorder has a substantial influence on magnetic behaviour. Both materials discussed above are ferro /ferrimagnetic without distinct difference in the Curie points of rare earth and iron sublattices.

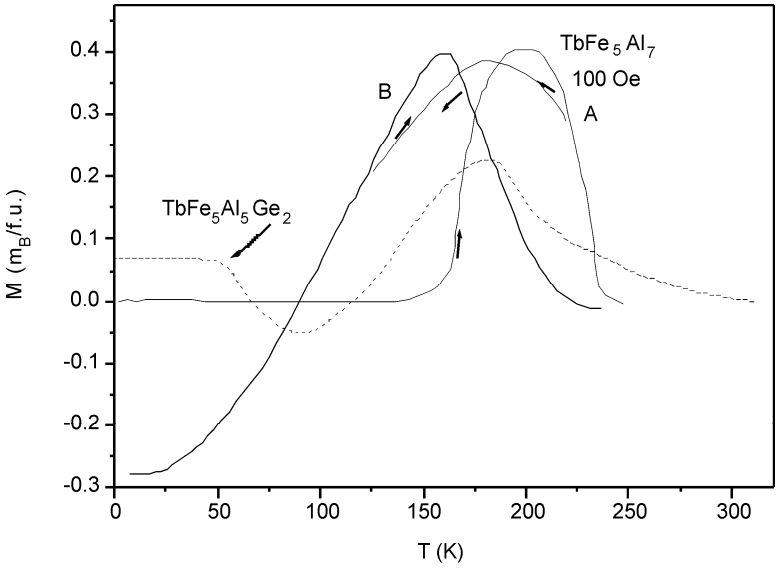

Fig. 2. Magnetization vs. temperature for $TbFe_5Al_7$ and $TbFe_5Al_5Ge_2$ [4]

A qualitatively similar behaviour is exhibited by $YbFe_4Al_8$ (Fig. 3 [1]) examined up to now in two different laboratories (in Wrocław [1] and Poznań [2, 3]) on polycrystalline alloys. As follows from Fig. 3, the zero field cooled (ZFC) sample behaves "normally" with a smooth decrease of the magnetic susceptibility, χ, on increasing temperature without any trace of anomaly at low temperature which could be an indication of the magnetic ordering in the Yb sublattice. Such a transition has been reported by Felner and Nowik [7] at 8 K. Our results demonstrate the maximum on the $\chi(T)$ plot at $T \sim 140$ K, corresponding to the Néel point of the Fe antiferromagnetic sublattice, which confirms the earlier results [7]. The $\chi(T)$ dependence for field cooled (FC) sample shows a different character with negative magnetic susceptibility below about 70 K and the maximum at about 140 K. Under slightly higher magnetic field, there is a fine anomaly (minimum) at about 15 K. Also, the anomaly has been detected in the $\chi(T)$ plot measured at 500 Oe and higher magnetic field but it is a maximum related to some paramagnetic impurities (ZFC) [3]. $YbFe_4Al_8$ has a perfect crystallographic structure (superstructure of $ThMn_{12}$ type), however, according to Drulis* a careful examination of the magnetic behaviour for samples with various

*Private communication.

stoichiometry revealed negative susceptibility only for some compositions close to the exact stoichiometry.

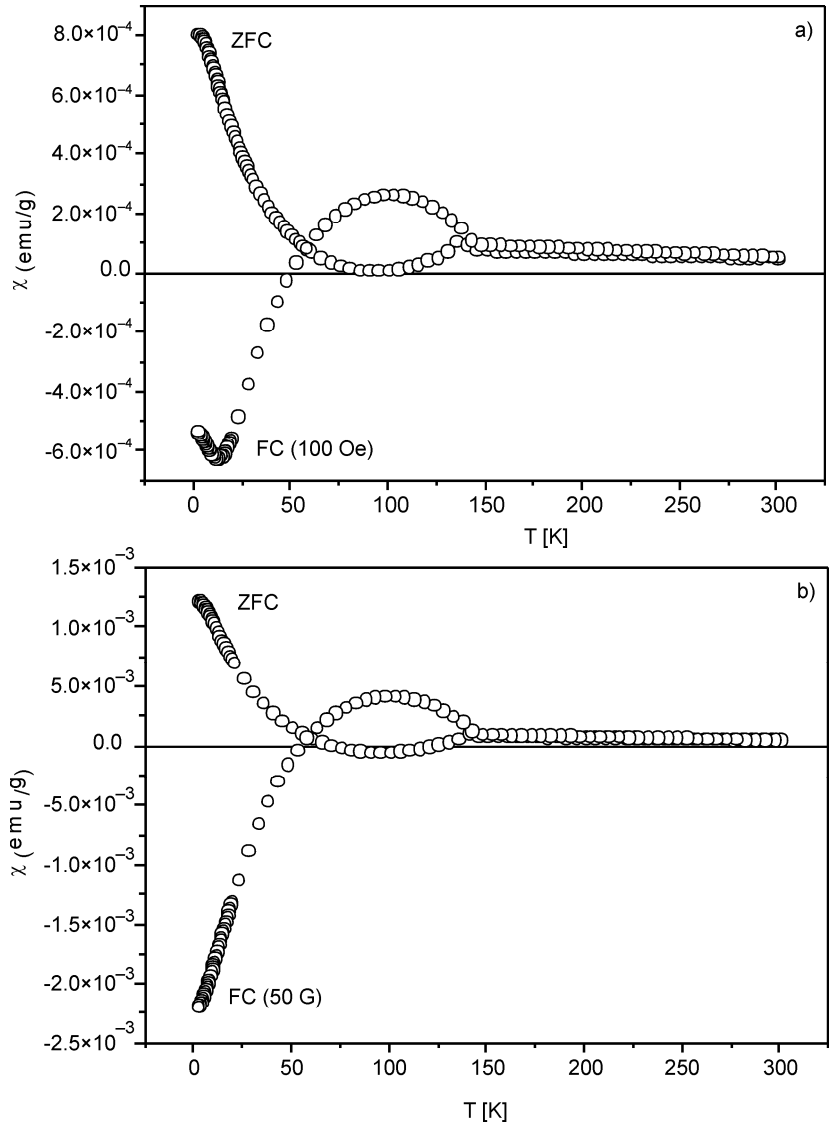

Fig. 3. ZFC and FC magnetic susceptibilities vs. temperature for polycrystalline $YbFe_4Al_8$ [1] in the magnetic fields of 100 Oe (a) and 50 Oe (b)

In Figure 4, the $\chi(T)$ dependence is shown for an imperfect single crystal sample. One can see that the negative magnetic susceptibility is absent, however, a clear difference between ZFC and FC runs is observed. The maximum in ZFC and anomaly in FC runs are seen at 24 K [8].

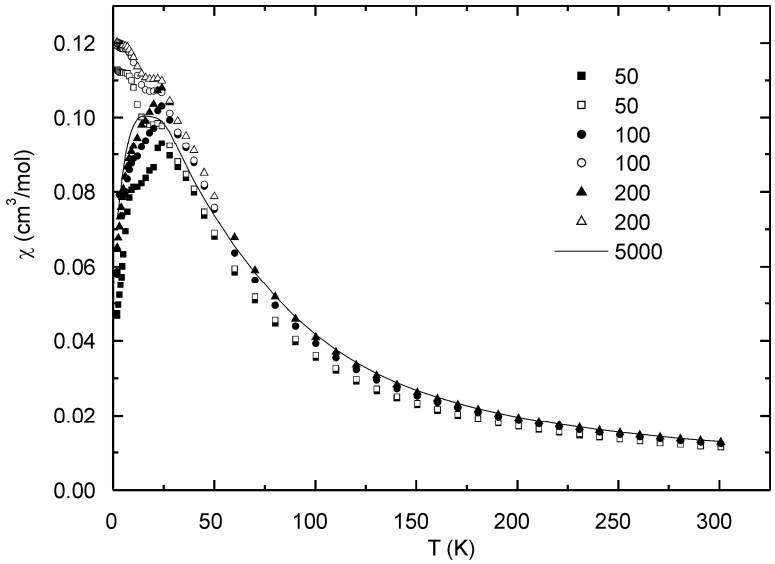

Fig. 4. Magnetic susceptibility vs. temperature for imperfect single crystal $YbFe_4Al_8$ [8]. Full symbols – ZFC, open symbols – FC

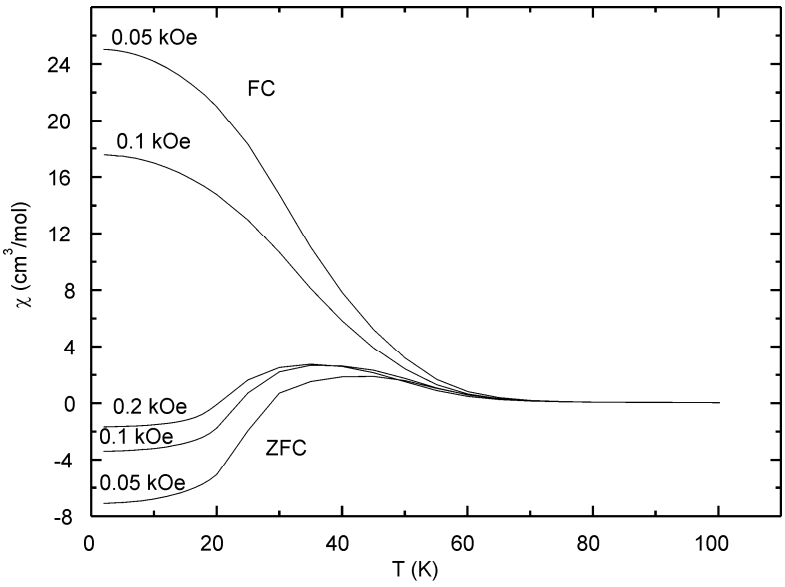

Fig. 5. Magnetic susceptibility vs. temperature for $UCu_{3.5}Fe_{1.5}Al_7$ [5]

Totally different behaviour is observed in the uranium pseudoternary alloy $UCu_{3.5}Fe_{1.5}Al_7$ [5]. This compound is supposed to be ferrimagnetic below 32 K [5], however, the transition was neither confirmed in the temperature dependences of the electrical resistivity [5] nor of the specific heat [9]. The temperature dependence of the magnetic susceptibility presented in Fig. 5 for the FC sample corresponds to

a "normal" ferri- or ferromagnet but for the ZFC sample, the magnetic susceptibility is negative below about 20 K, its absolute value decreasing with an increase of magnetic field. Although an approximate evaluation of the effective magnetic moment suggests that both U and Fe atoms carry magnetic moment, it does not mean that the magnetic ordering is established in both sublattices. The absence of two anomalies in the $\chi(T)$ dependence is not a serious argument for the absence of two magnetic sublattices because the spatial extent of the 5f shell can prevent creation of two separate magnetic transitions.

The next example of the negative magnetization is rhombohedral $Tb_{2.1}Co_{14.9}Si_3$ [6] which is ferro(ferri)magnetic below 623 K. At low temperatures, the temperature dependence of magnetization, $M(T)$, measured in magnetic field of 50 Oe (Fig. 6), exhibits the thermal hysteresis for all ternaries $Tb_{2.1}(Co,Si)_{17}$ but additionally a negative magnetization is seen below ~170 K in ZFC run and below ~90 K in FC run for $Tb_{2.1}Co_{14.9}Si_3$ alloy. However, in the latter case, the M(1.9K) value is apparently lower than the former one. It is worthwhile to note that such a behaviour was not observed in analogous Fe compounds [10–12]. Also the compounds of light rare earths and Co do not show negative magnetization [13]. Moreover, this behaviour seems to be connected with deeper crystallographic disorder growing with the increase of substitution of Si for Co. The contribution of the magnetically active atoms to magnetic ordering is not determined on the basis of the present preliminary investigations. The $M(T)$ plots exhibit an increase at low temperature upon heating but this can be related to the domain structure or a spin-glass state.

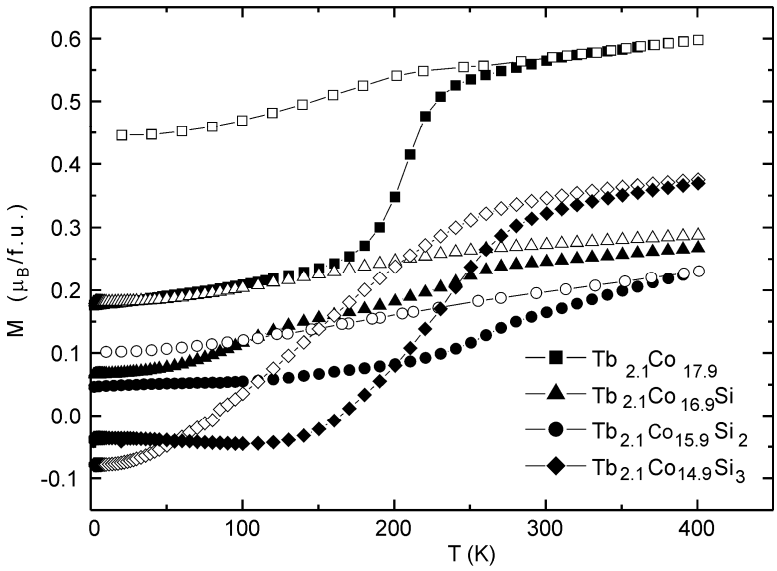

Fig. 6. Magnetization vs. temperature for $Tb_{2.1}Co_{14}Si_3$ [6].
Full symbols – ZFC, open symbols – FC

All above discussed materials crystallize in quite complicated crystal structures. Figure 7 shows the $ThMn_{12}$ type tetragonal structure (space group *I*/4*mmm*). Only exceptionally binary compounds exhibit this type of structure and as a rule ternaries are stabilized by alloying with other p or d electron elements. Forming of the ternaries is easy because there are 4 crystallographic sites available. In principle, for the RT_4Al_8 composition (superstructure) the 2(a) sites are occupied by the R (rare earth or actinide metal) atoms, the transition metal (Fe) is predominantly located in the 8(f) position and the Al atoms reside in the 8(i) and 8(j) sites. It is the picture which is assumed for the Yb compound, however for the compounds with the stoichiometry other than 4:8, 8(f) and 8(i) positions are occupied by the transition and Al atoms, respectively, while the remaining transition elements and Al atoms are distributed at random in 8(j) sites.

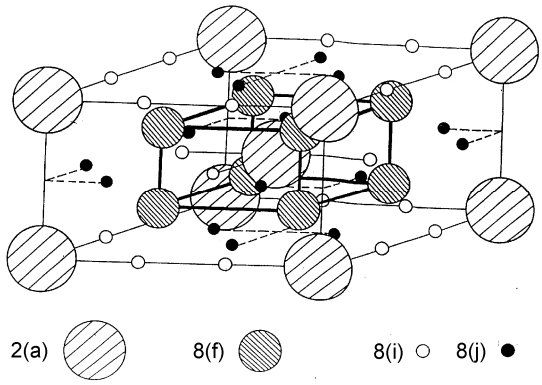

Fig. 7. The $ThMn_{12}$ type structure

The rhombohedral Th_2Zn_{17} type structure presented in Fig. 8 is even more complicated with a variety of available crystallographic positions. Different separation of the individual positions is a reason for the possibility of different types of magnetic interactions. At this point, it is worth mentioning that the type of magnetocrystalline anisotropy for the iron magnetic sublattice is axial whereas for the cobalt sublattice it is planar in the frequent cases. Therefore, such complicated crystal structures can be a reason for forming more than one magnetic sublattices which can be distinguished by different types and directions of magnetocrystalline anisotropy and by their various temperature dependences. The competition of these factors can create negative magnetization or magnetic susceptibility under favourable conditions.

Recently, negative magnetization for ZFC sample of UPdSb (hexagonal, $CaIn_2$ type, space group $P6_3/mmc$), ferromagnetic below 77 K has been reported [14]. In this case there is only one magnetic sublattice and therefore the reasoning presented above about the negative magnetization is not valid.

Summarizing, we can claim that the negative magnetization is observed in at least three groups of compounds. The first one is of ferrimagnetic ground state ($SmFe_5Al_7$, $TbFe_5Al_7$, $UCu_{3.5}Fe_{1.5}Al_7$ and $Tb_{2.1}(Co,Si)_{17.9}$), the other is of ferromagnetic one with

a strong magnetocrystalline anisotropy (UPdSb) and the last class includes $YbFe_4Al_8$, for which the magnetic ground state seems to be antiferromagnetic [1–3]. However, considering the presence of two magnetic sublattices (M1 and M2) in compounds belonging to the first group, one can find some ground for understanding their negative magnetization in the Néel theory [15].

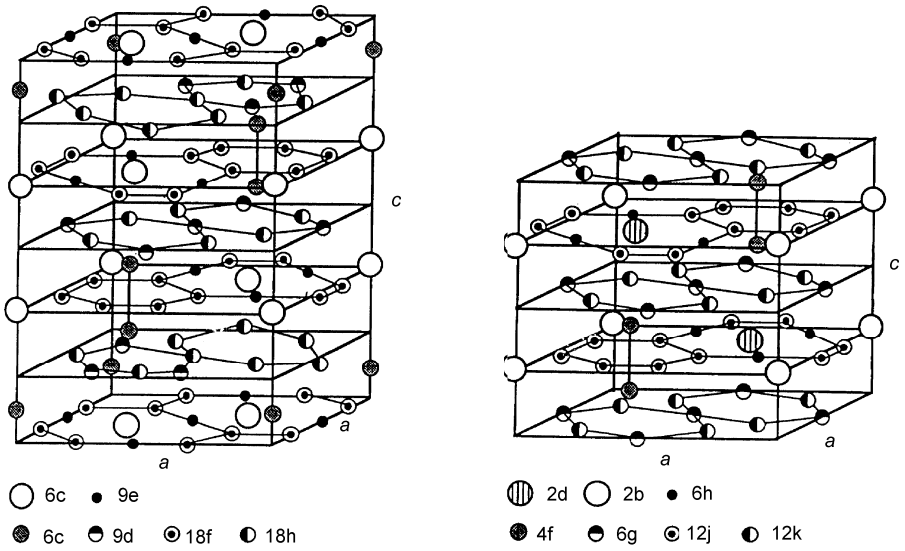

Fig. 8. The Th_2Zn_{17} type structure (left) and the Th_2Ni_{17} type structure (right)

Because M1 and M2 may have different temperature dependences, the total magnetization $M = [M1 - M2]$ is not ascribed to a Brillouin type shape, but strongly depends on history and measurement conditions. For the second group, the temperature dependence of magnetization can be explained in a similar manner as for ferrimagnets. The existing domain structure and/or anisotropy may act as the second magnetic sublattice. The behaviour of the Yb compound is less clear. Its magnetic susceptibility is strongly field dependent, even at temperatures clearly above T_N. This feature suggests that there exists a ferromagnetic correlation of unknown origin. Thus, one can suspect that Fe impurities may form ferromagnetic clusters being "imitation" of the second magnetic sublattice in ferrimagnets, and consequently they may contribute to the negative magnetization. However, the arguments presented above have speculative character and final conclusion can be formulated after further, more sophisticated experiments carried out on more perfect samples.

3. Conclusions

Summarizing, we can claim that the phenomenon of negative magnetization is not limited to one compound only, $YbFe_4Al_8$, but can be observed in other alloys, pre-

dominantly with $ThMn_{12}$ type structure. However, their stoichiometry is different from 4:8, this being a favourable condition for the creation of more than one magnetic sublattice. This observation allows one to point to the importance of stoichiometry and crystallographic excellence for physical properties.

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Received 7 May 2006
Revised 1 September 2006