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Journal of Alloys and Compounds 223 (1995) 237–241

Journal of
ALLOYS
AND COMPOUNDS

Comparison of structure and magnetic properties of the 4f and 5f electron $ThMn_{12}$-type ternary aluminides [☆]

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Abstract

The structure and magnetic properties of the $MeMn_xAl_{12-x}$ and $MeFe_xAl_{12-x}$ systems, where Me = rare earth or actinide, are presented. It is established that the magnetic order for the Mn compounds results from the antiferromagnetically coupled f-electron sublattice whereas in the Fe alloys both sublattices provide a contribution to magnetic order. In this case the complicated mutual relationships of various types of interaction can be a reason for the spin-glass state. For the actinide compounds strong hybridization might suppress magnetic order in the Mn compounds. The single magnetic transition for the aluminides with Fe is probably caused by the strong actinide–Fe interactions.

Keywords: Magnetic properties; Magnetic order

1. Introduction

Currently, a considerable amount of research concerning the $ThMn_{12}$-type f-electron-transition metal compounds is being carried out. This research was partially motivated by the possibility of obtaining new, promising magnetic materials. Before the detailed discussion, it should be mentioned that very few representatives of binaries are known, but ternaries or pseudoternaries can be grouped into two distinct families: the ternary aluminides of the MeT_xAl_{12-x} type where Me = rare earth (R) or actinide (An) and $3<x<6$ belong to one family and those of the $MeT_{12-x}M_x$ type in which the concentration of the transition element T is large, usually $x \approx 2$, and M corresponds to different, mostly transition elements belong to the other family. Because of the above-mentioned potential application of the second family, its structure and properties have recently been reviewed in many papers (see, e.g., [1]), and also for actinide compounds by the present author [2].

The aluminides, however, were discussed long ago [3,4]. Moreover, we have recently re-examined the structure and properties of the UMn_xAl_{12-x} [5] and UFe_xAl_{12-x} [6] systems and therefore a broader comparison of these materials with the rare earth analogues should be of interest.

Below we discuss the following problems: the stoichiometry, the crystal structure, phase equilibria and the occupation of the individual crystallographic positions, the most interesting magnetic and related properties, and finally the question of f-electron atom contribution to the magnetic properties of these materials.

2. Crystal structures and phase relations

The $ThMn_{12}$-type crystal structure is shown in Fig. 1. There are four non-equivalent positions available, of which the 2(a) positions are occupied by the f-electron atoms either by the rare earth or the actinide elements. For binary compounds, the other sites are available for the second component. Only very few binary compounds with Mn, Zn and Fe are known but a huge number of ternaries have been obtained with various elements stabilizing the structure. Except for $ThMn_{12}$ itself, all other binaries are formed by rare earths. The occupation of the remaining positions does not depend on the f-electron component but on the stabilizing atom (e.g. Mo enters the 8(i) position) and on the concentration of the transition element. The distribution of non-f-electron atoms has some influence on the magnetic properties of these materials. The total

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[☆] This paper is devoted to the memory of the late Jean Rossat-Mignod.

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SSDI 0925-8388(94)09006-8

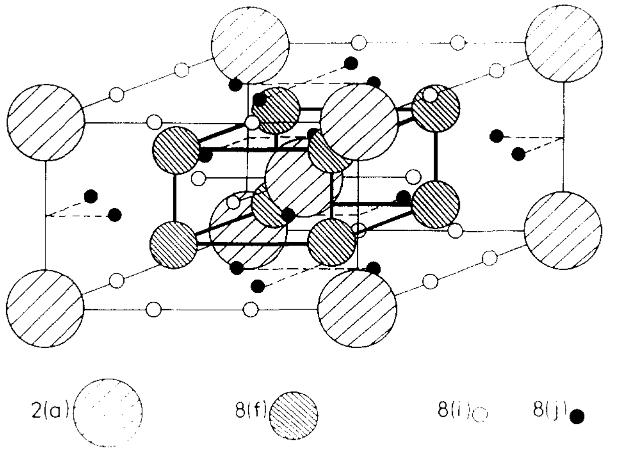

Fig. 1. ThMn$_{12}$ type of structure.

number of non-f-electron atoms in the unit cell is 24, but in numerous cases of rare earth compounds this number is smaller (for a review, see [7]). It seems that substoichiometry exists also in the actinide compounds. Although the deficiency of aluminium for UFe$_4$Al$_{8-x}$ reported by Gal et al. [8] was not confirmed in an examination of a single-crystal sample [9], the substoichiometry was proved in the case of UFe$_{9.2}$Si$_{1.8}$ single crystals [10].

The ThMn$_{12}$-type phase exists in a relatively narrow composition range. The closest neighbors are the BaAl$_4$ and Th$_2$Zn$_{17}$ type phases for compounds related to NdCu$_4$Al$_8$ [11].

As mentioned before, there are two types of phases, namely those with the MeT$_x$Al$_{12-x}$ type of stoichiometry (where T=Cr, Mn, Fe and Cu and instead of Al, Ga and In can be introduced) and MeT$_{12-x}$M$_x$, where T=Fe, Co and Ni and M=Si, Ti, V, Cr, Mn, Mo, W and Re. In the latter case, bulk actinide compounds are formed only with Si, and Mo and Re (T=Fe for Re and Mo). In the first group the uranium forms compounds of Mn, Fe and Cu with $x \leqslant 6$, but the lower limit of transition element is equal to 3, 3.5 and 4, respectively. For rare earths the concentration of the components is frequently complex [7].

In Fig. 2, the unit cell volumes for MeT$_4$Al$_8$ are presented according to [12,13]. One can see that the lanthanide compounds show in principle the lanthanide contraction, except for Ce compounds, and this behaviour probably results from a mixed valence state. This explanation might be valid also for YbCr$_4$Al$_8$. The actinide compounds present a monotonous decrease with increase in the actinide atomic number.

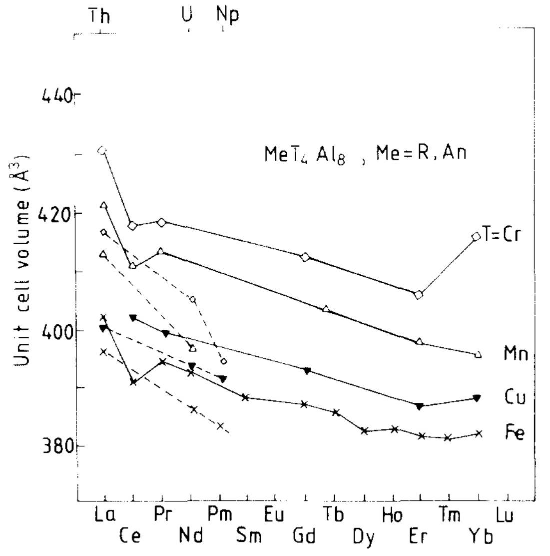

Fig. 2. Unit cell volume for MeT$_4$Al$_8$ ternaries, where Me=R or An and T=Cr (◇), Mn (△), Fe (×) and Cu (▼) [12,13].

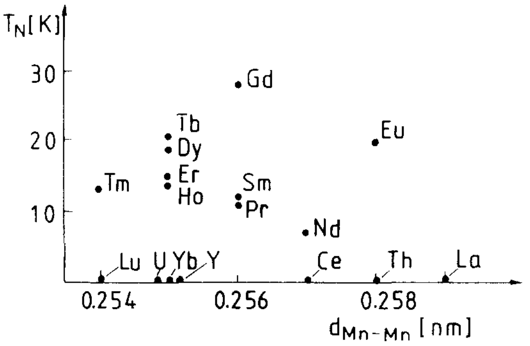

Fig. 3. Néel points of the MeMn$_4$Al$_8$ compounds, where Me=R or An, versus Mn–Mn separation (Mn in the 8(f) sites), d_{Mn-Mn}.

3. Existence range and magnetic properties

3.1. Compounds with T=Mn

The lanthanide aluminides with Mn are reported in the form of RMn$_4$Al$_8$ and RMn$_6$Al$_6$. However, we do not know whether systems with different stoichiometry exist or whether anyone has tried to obtain them. The majority of the RMn$_4$Al$_8$ compounds are antiferromagnetic at temperatures below about 30 K and the lack of magnetic ordering in the compounds of La and Lu and low Néel points are strong evidence that magnetic order is restricted to the lanthanide sublattice. The magnetic field of 1.7 T at 4.2 K induces a magnetic moment in the Mn sublattice which could be related to R–Mn interactions and these interactions could be the reason for an angle between the *c*-direction and the hyperfine field without external magnetic field as shown by Mössbauer effect (ME) examination [14] of some compounds. Szytuła [15] and Kim-Ngan et al. [16] tried to connect the magnetic ordering in the manganese–rare earth compounds with a critical Mn–Mn separation which for Laves phases is larger than 0.250 nm [16] and for some ternaries is >0.285 nm [15]. The Mn–Mn separation for the compounds considered here amounts to 0.254–0.259 nm. As can be seen from Fig. 3, the dependence of T_N on d_{Mn-Mn} does not demonstrate any regularity. On the contrary, for the same separation one can see different Néel points. Fig. 4 shows the Néel points of lanthanide compounds RMn_4Al_8 [14]. One can see that T_N versus lanthanide atomic number scales roughly with the de Gennes factor $(g_J-1)^2j(J+1)$, similarly to the relationship shown for RCu_4Al_8 systems [14], and this plot is also strong evidence of the exclusive rare earth contribution to the magnetic order.

The RMn_6Al_6-type compounds are known only for the heavier lanthanides and Y. They seem to be weak ferromagnets with ordering temperatures below 15 K and low saturation moments reaching at most 2.1 μ_B/fu for the Dy aluminide. One cannot discuss the critical distances of the Mn atoms in these alloys because the lattice parameters and the Mn atom distribution are not known [17]. ^{155}Gd ME examination [17] revealed for $GdMn_6Al_6$ an angle between the hyperfine-field direction and the c-axis. In Fig. 4 the T_C points are presented for the RMn_6Al_6 compounds, demonstrating the scaling with the de Gennes factor.

The UMn_xAl_{12-x} system exists in the broad concentration range $3 \leqslant x \leqslant 7$ as the single phase. In contrast to the lanthanide analogues, UMn_4Al_8 and the alloys with $x>4$ are paramagnetic down to 4.2 K [5,18], but UMn_3Al_9 exhibits a magnetic ordering at ca. 30 K. The arguments applied to the compounds of magnetic lanthanide aluminides support the assumption that the uranium sublattice is ordered for Mn-deficient samples. The paramagnetic behaviour of other uranium samples is probably related to hybridization of magnetic 5f electrons, which suppresses magnetic order.

3.2. *Compounds with T = Fe*

The $MeFe_4Al_8$-type compounds are the most frequently investigated representatives of aluminides. Only for these systems were monocrystalline materials obtained [9,10,19–23] and a comparison of data obtained with such samples is, therefore, most reliable. Unfortunately, the rare earth compounds available as single crystals are not close analogues of the thorium, uranium or neptunium compounds. The salient feature of the lanthanide compounds which distinguishes them from actinide materials is the observation of two transition temperatures for the former materials whereas the latter exhibit only one transition point. This is an indication that the interaction between the actinide and transition metal is much stronger than that between the lanthanide and the transition metal. According to neutron diffraction (ND) and ME experiments, the Fe sublattice is ordered antiferromagnetically at 100–200 K, whereas the f-electron sublattice is ordered ferromagnetically below ca. 10–40 K, and the easy direction is located in the (a, b) plane. In some cases, however, the easy direction is tilted with respect to the c-axis direction (e.g. in the Eu compound $\delta=65(5)°$, in the Gd compound $\delta=44(2)°$ and in the Yb compound $\delta=40(5)°$ [14]). In spite of the antiferromagnetic ordering of the Fe sublattice, a small ferromagnetic moment at 4.2 K and 1.7 T was observed in the compounds of Y, La, Ce and Lu [24], and also in single crystals of YFe_4Al_8 [21]. The spin-glass (SG) state has been reported for the compounds of Dy [23], Ho [23], Y [21,23] and U [8], and for the rare earth compounds also in the single-crystal form. For UFe_4Al_8, however, a recent single-crystal examination did not confirm the SG state [9]. The preferential occupation of the 8(f) position by the Fe atoms was established by ^{57}Fe ME for U [6,8], Gd [25], Er [26], Tb [27] and Y [28] compounds.

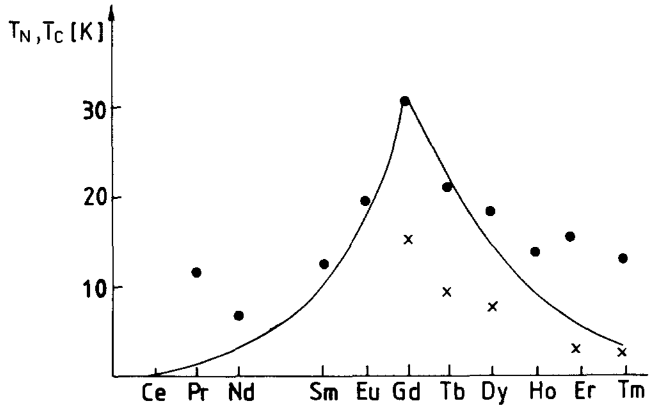

Fig. 4. Néel points of RMn_4Al_8 (●) and the Curie points of RMn_6Al_6 (×) versus atomic number of lanthanide atom [14]. The solid line is proportional to the de Gennes factor $(g_J-1)^2J(J+1)$.

Let us now inspect the $MeFe_xAl_{12-x}$ systems. Among the actinides these exist in a broader concentration range: $4 \leqslant x \leqslant 5$ and $3<x<6$ for Np and U compounds, respectively.

For the rare-earth alloys, the most detailed examination has been carried out for compounds of Gd, Tb, Er and Y. The existence range is different for different 4f metals. For example, for Gd and Dy compounds Wang et al. [29] reported on alloys with $x=8$ and $x=10$ obtained by melt-spinning. The samples, however, contained some amount of free α-Fe. An introduction of subsequent Fe atoms for $x>4$ causes an occupation of other sites, mostly 8(j) [28,30]. It has been reported [26] that for $x=6$, for R = Er only 33% of Fe atoms remain in 8(f) whereas for Tb [27] and Y [28] no Fe atoms stay in this position. For $GdFe_{10}Al_2$ [31] the 8(f) and 8(i) sites are fully occupied by iron, whereas the 8(j) site is equally occupied by Fe and Al.

The RFe_5Al_7 compounds are ferrimagnetic below ca. 200 K, as was shown by neutron diffraction experiments [32] and magnetic measurements [33], revealing a minimum in the temperature dependence of magnetization at 29–40 K. However, these alloys demonstrate an unusual behaviour in many respects, e.g. time-dependent magnetization and huge hysteresis in the field and temperature dependence of magnetization [3]. Recently, Halevy et al. [34] have shown that two magnetic transitions are present in $HoFe_5Al_7$. Below the upper transition at 200 K, long- and short-range magnetic order co-exist, whereas below ca. 60 K the onset of long-range order is indicated. In turn, both U and Np compounds are ferromagnetic below 260 K [6] and 250 K [34], respectively.

The RFe_6Al_6 systems are also reported to be ferrimagnetic below ca. 300–350 K, but instead of the above-mentioned minimum, a maximum in the temperature dependence of magnetization was observed even in the Y compounds [28]. According to ND, UFe_6Al_6 is ferromagnetic [35].

Since there is no difference between the Curie points of the compounds with magnetic and non-magnetic rare-earth elements (uranium), the contribution of the f-electron metal to the magnetism is difficult to determine. We tried to do this by inspecting the difference between magnetic moments of the Y and lanthanide (uranium) compounds and the difference in magnetic moments determined in magnetometric and ^{57}Fe ME measurements. In both cases the difference should correspond roughly to the magnetic moment of the f-electron element sublattice. The incomplete data, however, allow for such a procedure only for Dy and U compounds. For Dy aluminide the value resulting from a comparison of ME and magnetization examinations seems to be unrealistic (0.27 μ_B/fu), whereas the relationship to the Y compound provides a much more realistic value of 6.93 μ_B per Dy atom. In turn, there are two values of 1.34 and 1.56 μ_B per U atom for uranium, but both are lower than the ND result, the latter being 2.1 μ_B per U atom [35]. Fig. 5 shows the values of the magnetic moment determined in magnetometric measurements, M_s, the values of the magnetic moment of the Fe sublattice, M_{Fe}, the magnetic moment determined in ND experiment for UFe_xAl_{12-x} [6] and the magnetic moment of the Fe sublattice in the YFe_xAl_{12-x} obtained from ME [28] versus Fe concentration, x. It is seen that for U alloys of low Fe concentration, M_{Fe} slowly increases with increase in x, but for $x=5$ and 6, when the Fe atoms enter positions other than 8(f), M_{Fe} increases more rapidly. The x-dependence of the saturation moment, M_s, is irregular. Again, for low x the M_s changes weakly with the Fe concentration but for $x=4$ there is a clear minimum corresponding to compensation of the iron moment in the AF sublattice. Thus, the observed value is the magnetic moment of the uranium ferromagnetic sublattice, very close to the value determined in the ND examination [36]. The subsequent strong increase is due to the Fe atoms entering other than 8(f) sites. However, the difference between the value of the total magnetic moment and that obtained from the ME for the Fe sublattice is smaller than the ND value. The magnetic moments of the Fe sublattice of YFe_xAl_{12-x} obtained from ME [28], as one would expect, roughly correspond to those of UFe_xAl_{12-x} [6]. The contribution of the Tb sublattice to the magnetism of the $TbFe_xAl_{12-x}$ alloys is considered as the reason for the high anisotropy and the SG state [27] below relatively high transition temperatures. In turn, the contribution of Er in the $ErFe_xAl_{12-x}$ alloys does not cause the formation of an SG state, but complicated phase relations result from the fact that the Er sublattice is ferromagnetic like that of uranium, but unlike U it is antiferromagnetically coupled to the Fe sublattice [26]. As Er belongs to the second half and U to the first half of an f-series, a different type of coupling occurs. The Fe sublattice, depending on concentration, x, and temperature, can be ferro- or antiferromagnetic. Moreover, ferromagnetic clusters may exist in the AF matrices. However, the statement about the AF coupling of the Er sublattice to the Fe AF sublattice sounds strange. Such a type of coupling can exist only for $x \approx 6$ where the Fe sublattice is ferromagnetic.

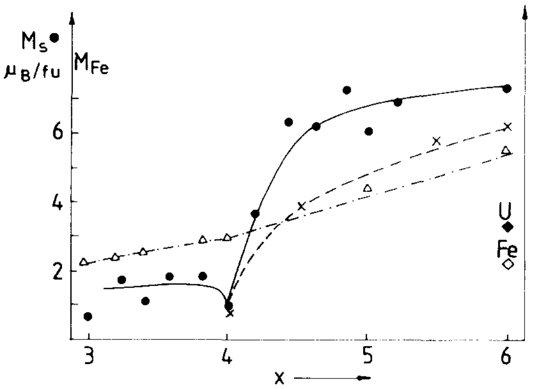

Fig. 5. Saturation magnetic moment M_s for UFe_xAl_{12-x} (●) systems [37] and magnetic moment of the Fe sublattice, M_{Fe}, for UFe_xAl_{12-x} (△) [6] and for YFe_xAl_{12-x} (×) [28], determined by ^{57}Fe ME, and magnetic moments determined in ND for U (◆) and Fe (◇) [35,36].

4. Conclusions

The systems discussed exhibit complex magnetic behaviour. It is well established now that in Mn compounds the f-electron element is responsible for the magnetic (antiferromagnetic or weak ferromagnetic) order. In uranium compounds, however, this order is suppressed by strong hybridization, although magnetic order in the U sublattice is formed for the lowest concentration of Mn.

For the Fe compounds, magnetic order exists in both sublattices. A ferromagnetic order is set up in the f-electron element sublattice whereas the type of magnetic order in the Fe sublattice depends strongly on stoichiometry and sometimes on temperature. The competition of various magnetic interactions can produce a spin-glass state, observed in some of the systems.

Because of technological problems, this observation needs further investigation. Recent success in growing single crystals is a good starting point for the final elucidation of structure and properties of these materials.

Acknowledgements

I gratefully acknowledge the collaboration with my colleagues and co-workers H. Drulis, T. Mydlarz, F.G. Vagizov and K. Wochowski. I have also profited from discussions with A.V. Andreev and J. Gal.

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