# Heat capacity of amorphous, partly crystalline and polycrystalline $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($0 \le x \le 6$) system

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We present heat capacity measurements of $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($0 \le x \le 6$) in ordered and disordered crystalline states in the magnetic fields up to 9 T and in the temperature range 1.7-200 K to discuss their dependence on structural disorder. Samples in the shape of ribbons were synthesized by a single-roller rapid quenching technique. Starting from the hexagonal alloy $DyMn_6Ge_6$ ($TbCu_7$-type structure), the partial substitution of Mn and Ge by Fe and Al leads to the formation of metallic glasses (x = 0 - 2.5), partially (x = 3) or fully ordered alloys (x = 4, 5, 6) in the rapid quenches. The electronic coefficient $\gamma_{eff}$ varies from 70 to about 400 mJ $mol^{-1}$ $K^{-2}$ for x=2.5 and 4, respectively, and depends only weakly on stoichiometry, but it depends strongly on structural disorder. Such dependence confirms also our preliminary study on amorphous and partly crystallized $Y_{50}Cu_{42}Al_8$ alloys without any magnetic component.

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## 1. Introduction

Recently the structural transition from a tetragonal intermetallic compound to a hexagonal compound and related complex magnetoresistive and magnetic properties have been studied in the pseudoternary series $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($0 \le x \le 6$) [1]. Physical properties of the pure limiting (x = 0, 6) ternary intermetallics of the $R–T_6–M_6$ (R: rare earth, T: transition metal, M: metalloid) type are well-known, see *e.g.* [2]. The intermetallic compound $DyMn_6Ge_6$ crystallizes in the hexagonal $HfFe_6Ge_6$-type structure (P6/*mmm*) [3,4]. It shows a magnetic order transition at $T_N$ = 423 K [5] into a state with macroscopically antiferromagnetic properties. Both the Mn-sublattice and the Dy-sublattice order simultaneously in this compound. The spin-structure has been determined as a flat ferrimagnetic incommensurate helix, i.e. with a locally antiferromagnetic coupling between Dy and Mn sites [6]. Below about 100 K, the spin-structure undergoes a transition into a triple conical helix [3,4]. The substitution of MnGe by FeAl leads to the formation of a disordered $CeMn_4Al_8$-type structure (*I4/mmm* space group) with a ferrimagnetic ordering transition at $T_C$ = 340 K for $DyFe_6Al_6$ [7, 8, 9]. There is a further magnetic transition or anomaly at 130 K reported in [10] which is not well understood yet. Starting from the rapidly quenched $DyMn_6Ge_6$ alloy with a metastable hexagonal $TbCu_7$-type structure, it was recently found that a partial substitution of Mn and Ge by Fe and Al, leads to destabilization of the crystalline structure and to the formation of amorphous states in rapid quenches [1]. The structural characterization by X-ray diffraction (XRD) of these samples was published in details already [2]. The magnetization measurements of $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($0 \le x \le 6$) samples show the dependence of magnetic properties on the structural state, which can be amorphous, nanocrystalline, or coarsely polycrystalline [2]. The mechanism of glass formation in these alloys was also studied and described in Ref. [3].

In order to gain more insight into basic properties of these metastable alloys, we have measured specific heat on the series of amorphous and polycrystalline $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($0 \le x \le 6$) samples. As is well known, glassy states generically display excess specific heat contributions at low temperatures that grow linearly with temperature, $\Delta C \sim T$ [11]. Our samples are metallic, magnetically ordered al low temperatures, and the *4f* shell of Dy may contribute Schottky-like specific heat contributions from excitations into levels split by the crystalline electric field (CEF) and the magnetic exchange field. These different contributions cannot be easily disentangled. However, we find that the structural disorder yields an enhanced coefficient of the linear contribution to the specific heat, $C = \gamma_{\text{eff}} T$.

## 2. Experimental

Samples of $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ series with x = 0 - 6 have been prepared in ribbon shape by arc-melting and melt-spinning. Details of preparation and characterization

of samples are described in Refs 1, 2 and 3. Chosen samples were also isothermally annealed.

Heat capacity measurements were performed by PPMS Quantum Design commercial device in the temperature range 1.7 – 300 K and in applied magnetic field up to 9 T using the two-tau model.

## 3. Results

Previous analysis of XRD measurements have shown that samples with composition x = 0.5, 1, 1.5, 2, 2.5 are in amorphous states but with x = 0, 4, 5, and 6 are polycrystalline [2]. Alloys with x = 3, 4, 5 are not single phase materials, that means at least two crystalline phases were detected for x= 4 and 5 but in sample x = 3 crystalline grains are embedded in the amorphous matrix. Temperature dependence of heat capacity of polycrystalline $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ samples without applied magnetic field below 200 K, are presented in Fig. 1. The heat capacity of amorphous $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ (x = 0.5, 1, 1.5, 2, 2.5) samples is shown in Fig. 2.

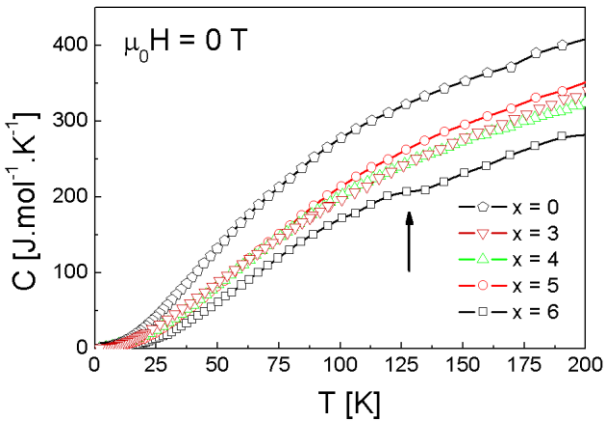


*Fig. 1. Temperature dependence of heat capacity of polycrystalline $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($0 \le x \le 6$) samples in magnetic field $\mu_0H$ = 0 T. Arrows indicate an anomaly described in the text.*

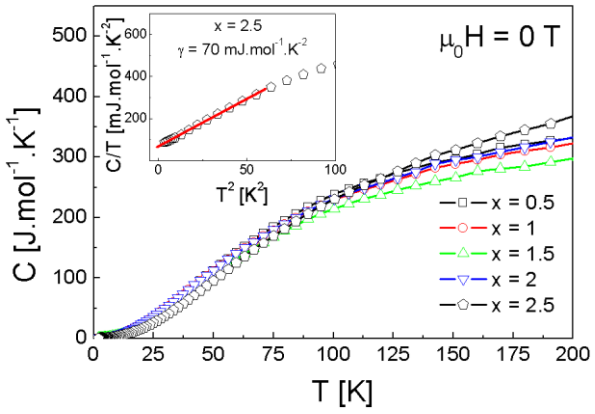


*Fig. 2. Temperature dependence of heat capacity of amorphous $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($0 \le x \le 6$) samples in magnetic field $\mu_0H$ = 0 T. Linear fit of the low temperature part of specific heat in $CT^{-1}(T^2)$ coordinates is presented in the inset.*

We did not observe signs of magnetic transition at temperatures below 200 K. They are expected above 350 K except for $DyFe_6Al_6$. However, for $DyFe_6Al_6$ we have observed a shoulder at 127 K, which well coincide with anomaly of unknown origin at 130 K reported in [12].

Due to expectation of magnetic contributions to the heat capacity of all $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$, we have made measurements in the applied magnetic field $\mu_0H$ = 9 T (Figs. 3 and 4 for polycrystalline and amorphous samples, respectively). We have observed negligible influence of magnetic field. There is probably necessity to apply much higher magnetic field to influence this contribution.

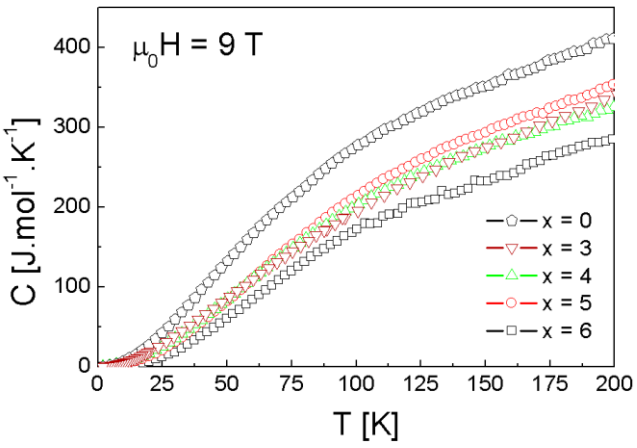


*Fig. 3. Temperature dependence of heat capacity of polycrystalline $DyMn_xGe_xFe_{6-x}Al_{6-x}$ ($0 \le x \le 6$) samples in magnetic field $\mu_0H$ = 9 T.*

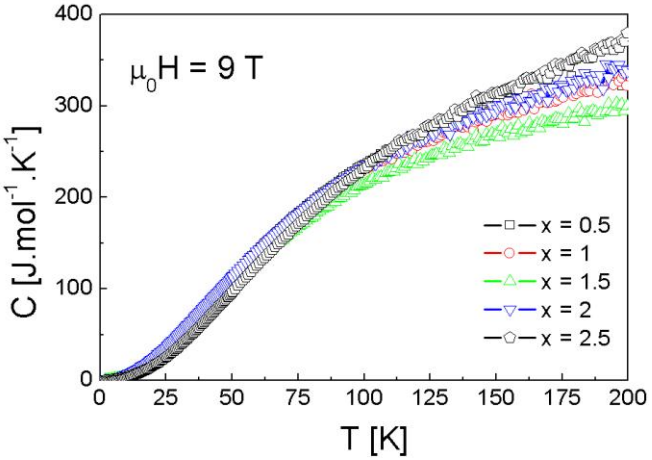


*Fig. 4. Temperature dependence of heat capacity of amorphous $DyMn_xGe_xFe_{6-x}Al_{6-x}$ ($0 \le x \le 6$) samples in magnetic field $\mu_0H$ = 9 T.*

In order to determine the effective Sommerfeld electronic coefficient $\gamma_{eff}$, connected with electronic contribution to heat capacity, we performed standard procedure by plotting $C(T)/T$ *vs.* $T^2$ (for example see the inset of Fig. 2). The results are summarized in Table 1.

*Table 1. Electronic heat capacity coefficient $\gamma_{eff}$ of $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($0 \le x \le 6$) in $\mu_0 H$ = 0 T and 9 T.*

| x | 0 | 0.5 | 1 | 1.5 | 2 | 2.5 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|---|---|---|
| am – amorphous<br>cr – polycrystalline | cr | am | am | am | am | am | am + cr | cr | cr | cr |
| | $\gamma_{eff}$ (± 5) in mJ mol$^{-1}$ K$^{-2}$ | | | | | | | | | |
| $\mu_0$H = 0 T | 235 | 224 | 226 | 220 | 239 | 70 | 166 | 397 | 100 | 82 |
| $\mu_0$H = 9 T | 211 | 225 | 230 | 220 | 234 | 70 | 160 | 161 | 94 | 67 |

To take into account the possible magnetic field contribution at low temperatures we determined $\gamma_{eff}$ also in an applied field of 9 T. Magnitudes of Sommerfeld coefficient can be discussed after separation into three groups. The amorphous alloys and polycrystalline but structurally metastable $DyMn_6Ge_6$ with a disordered hexagonal $TbCu_7$-type structure (space group *P*6/*mmm*) have $\gamma_{eff}$ values around 220 mJ mol$^{-1}$ K$^{-2}$ and higher than crystalline samples x = 5 and 6 (100 and 82 mJ mol$^{-1}$ K$^{-2}$, respectively). Third group of samples with x = 2.5, 3 and 4 shows anomalous behaviour, with exceptionally small values of $\gamma_{eff}$ for fully amorphous sample with x= 2.5. The magnitudes of $\gamma_{eff}$ are rather high comparing to simple metals. For the crystalline $DyMn_6Ge_6$ (x=0) and for the crystalline compounds with $4 \le x \le 6$, the magnetic field has a discernible or even strong effect. For $DyMn_6Ge_6$ this is understandable as there should be a spin-wave contribution $C_{sw} = B_{3/2} T^{3/2}$ in this effectively ferrimagnetic compound. This contribution is difficult to discern from the proper electronic specific heat of a metal $C = \gamma T$, but it can be suppressed by magnetic fields. However, we were not able to separate $C_{sw}$ from the measured curves. Spin wave contributions to specific heat may also underlie the strong effects for large x. For other alloys with amorphous structures, the applied magnetic field seems not strong enough to substantially influence the magnetic contribution to the heat capacity, but from this fact the presence of magnetic contribution can not be excluded. The *4f* level excitations in Dy also can produce smooth low –temperature excess contributions in the disordered samples owing to distributions of CEFs and varying magnetic exchange fields, *e.g.* if there are first excited levels in the range up to 100 K in energy. But, main possible origin of high $\gamma_{eff}$ value is the contribution of structural disorder which produces higher entropy $S = \int C/T\, dT$. For x = 4 even strong anomalies in $\gamma_{eff}$ values are observed. This could be connected with the proximity of composition range, where the glass forming ability is increased. In this composition range the samples are multiphase mixtures consisting of partially amorphous and ultrafinely grained polycrystalline structures.

Heat capacity measurements of partially crystallized samples (after heat treatment) were also performed to confirm the influence of structural disorder on the specific heat coefficient $\gamma_{eff}$. All amorphous samples were isothermally annealed above crystallization temperatures. For example $DyM_{4.5}Ge_{4.5}Fe_{1.5}Al_{1.5}$ was annealed at 490°C and 510°C for 15 minutes. During the process, creation of multiphase crystalline structure occurs. Due to the ordering there are significant changes in $\gamma_{eff}$. Its value decreases from 220 mJ mol$^{-1}$ K$^{-2}$ for fully amorphous sample to 159 mJ mol$^{-1}$ K$^{-2}$ and finally 84 mJ mol$^{-1}$ K$^{-2}$ for the samples annealed at 490°C and 510°C, respectively. The origin of such behaviour is structural ordering which gives rise to the lowering of density of states in the vicinity of Fermi level and decreasing of electron effective masses. Very similar trend was observed for other multicomponent amorphous sample with stoichiometry $Y_{50}Cu_{42}Al_8$ (and also in different nanocrystallized states) produced and investigated in our laboratory.

## 4. Conclusions

We have studied the temperature dependences of heat capacity in structurally metastable $DyMn_xGe_xFe_{6-x}Al_{6-x}$ ($0 \le x \le 6$) alloy series. The heat capacities in the temperature range 1.7 - 200 K do not display remarkable differences between ordered and disordered forms and effects of magnetic fields up to 9 T are weak. Changes of $\gamma_{eff}$ value for isothermally annealed samples confirm that structural disorder is the most important factor that affects $DyMn_{6-x}Ge_{6-x}Fe_xAl_x$ ($0 \le x \le 6$) thermal properties. This result corroborates the glassy disordered structure of these materials. The weak dependence on magnetic field suggests that vibrational modes in these metallic glasses are responsible for the enhanced $\gamma_{eff}$. It was confirmed by us (unpublished results) on samples without magnetic element like lanthanide or transition metal. Even more, conclusion from these investigations forced us to systematic study of $\gamma_{eff}$ dependence *vs.* different crystalline states from fully amorphous *via* nanocrystalline forms, with different crystallized volume fractions, to fully polycrystalline $Y_{50}Cu_{42}Al_8$ [13] and $Y_xCe_{50-x}Cu_{42}Al_8$ ($0 \le x \le 50$) samples.

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