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The Influence of Thermal Treatment on Magnetic Moments in *i*-Al-Pd-Mn Quasicrystals*

Marko Jagodič,[a,] Zvonko Jagličić,[a,b] Benjamin Grushko,[c] and Janez Dolinšek[d]**

[a]*Institute of Mathematics, Physics and Mechanics, Jadranska 19, SI-1000 Ljubljana, Slovenia*
[b]*Faculty of Civil and Geodetic Engineering, University of Ljubljana, Jamova 2, SI-1000 Ljubljana, Slovenia*
[c]*Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany*
[d]*Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia*

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Abstract. The influence of cooling rate on thermal strains in the quasicrystalline icosahedral Al-Pd-Mn complex metallic alloy was investigated. In general, measurements of the electronic magnetization can be used as an indirect method for determining the short-scale disorder in the crystal structure as the magnetic moments at the Mn sites are highly dependent on their local environment. Excluding the contributions of thermal vacancies and second phase precipitates by proper selection of preannealing temperatures and durations, the changes in magnetization can be ascribed to the appearance or disappearance of thermal strains in the crystal structure. It was found that water-quenching increases thermal strains irrespective of previous thermal history.

Keywords: complex metallic alloys, quasicrystals, thermal annealing, structural order, thermal strains, magnetic properties

INTRODUCTION

Structural order of crystals can be improved by thermal annealing, where diffusion of atoms at high enough temperatures relaxes the crystal structure. To preserve this relaxed structure the samples are often rapidly cooled by water-quenching (WQ) to room temperature (r.t.). However, such sudden changes in temperature can cause large temperature gradients resulting in quenched-in thermal strains. To avoid these problems slow cooling (SC) can be employed. However, this procedure is only valid if the alloy system does not contain additional low-temperature equilibrium phases for the particular chemical composition.

The short scale disorder (up to about 5–10 Å) in *i*-Al-Pd-Mn can be indirectly studied by measurements of the electronic magnetization as the magnetic state of Mn atoms is highly dependent on their environment.[1–3] Namely, the Mn atoms are close to the magnetic/non-magnetic transition as their magnetic moments are determined by the local density of states (DOS) which was shown to be strongly dependent on the Mn local environment and even on the environment up to 5–10 Å.[3] Already a small redistribution of atoms or vacancies near a Mn atom can induce the appearance or disappearance of the magnetic moment at that site. The introduction of thermal vacancies and strains into the structure thus influences the magnetization of the sample. The appearance of secondary phase precipitates can also change the magnetic properties of the material. To study only the contributions of thermal strains the sample must be properly preannealed. The annealing temperature and duration must be high enough for thermal vacancies reaching thermal equilibrium, where the majority of the vacancies are aggregated into few large voids.[4] Furthermore, there must be no secondary phase precipitates present in the material at the annealing temperature. The aim of the present work is to investigate under what annealing conditions thermal strains appear in the crystal structure and to determine the extent of their influence on the magnetic properties of the material.

EXPERIMENTAL

A bar-shaped single-crystalline *i*-Al-Pd-Mn sample of $\approx 1\times1$ mm^2 cross-section and a length of few mm was cut from an ingot grown by the Bridgman technique. The alloy for the crystal growth was prepared by levitation melting in a cold Cu crucible under Ar

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** Author to whom correspondence should be addressed. (E-mail: marko.jagodic@imfm.uni-lj.si)

atmosphere from elementary components. The purity of the initial materials was 99.999 % for Al, 99.95 % to 99.99 % for Pd and 99.99 % for Mn. The Al and Mn pieces were etched before melting. The crystal growth was carried out under an Ar atmosphere. The composition of the resulting sample, determined by inductively coupled plasma optical emission spectroscopy, was $Al_{70.1}Pd_{21.4}Mn_{8.5}$ with the uncertainty of 0.5 % with respect to fractions of atoms. Then the sample was preannealed in an evacuated quartz ampoule for 3640 h at 800 °C followed by cooling at a low cooling rate. The sample was cut into two approximately equal pieces using spark erosion and mechanically polished to remove damaged surface layers due to cutting. After each subsequent heat treatment, the surfaces of the two samples were slightly repolished.

Measurements of the electronic magnetization *versus* external magnetic field, $M(H)$, and magnetic susceptibility *versus* temperature, $\chi(T)$, were carried out using a commercial Quantum Design MPMS XL-5 magnetometer. The $M(H)$ curves were measured at T = 5 K by varying the magnetic field from 0 T to 5 T. The $\chi(T)$ curves were measured in a magnetic field H = 1 T and in the temperature interval between 2 K and 300 K.

The measured $M(H)$ curves were fitted using the expression

$$M = M_S B_J + \chi_{LIN} H \tag{1}$$

where B_J is the Brillouin function describing the magnetization of localized paramagnetic moments with angular momentum J. Furthermore, M_S is the saturation magnetization and χ_{LIN} is the magnetic susceptibility associated with contributions linear with the magnetic field H (Larmor diamagnetism, Pauli paramagnetism due to conducting electrons and contribution of localized moments with small enough magnetic moments for which $M \propto H$ up to 5 T). In the analysis we set J = 5/2 due to Mn^{2+} ions which posses the highest possible magnetic moment.[5] The measured $\chi(T)$ curves were fitted by the Curie-Weiss law including a temperature-independent term χ_0:

$$\chi = \chi_0 + \frac{C}{T - \theta} \tag{2}$$

The constants C and θ are the Curie constant and the Curie-Weiss temperature, respectively. From the C the mean effective Bohr magneton number per Mn atom $\overline{p}_{eff}$ could be calculated using the formula $\overline{p}_{eff} = 2.83\sqrt{C}$.[6] For the comparison of the electronic magnetizations after thermal treatment we used the normalized mean effective magnetic moment per Mn atom (for brevity called just normalized moment in the following) $m = \overline{p}_{eff} / p_{eff}$, where p_{eff} is the effective Bohr magneton number of bare Mn^{2+} with the value of $p_{eff} = 5.9$.[5]

RESULTS AND DISCUSSION

First, magnetic measurements were carried out on the preannealed sample, denoted by PA. The $M(H)$ and $\chi(T)$ curves are displayed in Figures 1 and 2, respectively. Parameters obtained by fitting the curves using Eqs. (1) and (2) are listed in Table 1. For the PA sample the normalized moment $m_{PA} = 3.1\times10^{-2}$ was obtained. In the next step, the sample PA was cut into two pieces, denoted by sample A and sample B, and both were further annealed at 800 °C for times short enough[4] not to influence the vacancy concentration anymore. However, the samples were cooled to room temperature

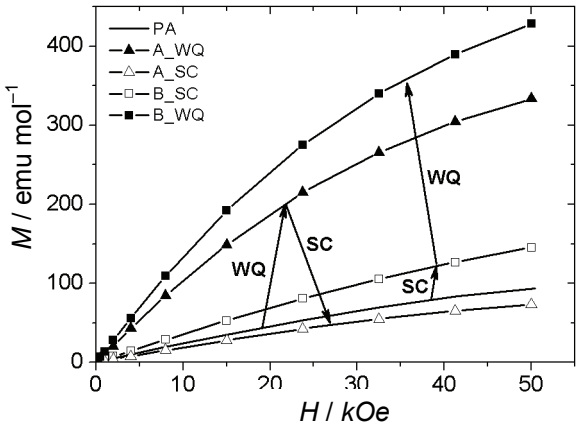

Figure 1. Magnetization *versus* magnetic filed curves measured at T = 5 K. The arrows in the panel show succession of annealing steps.

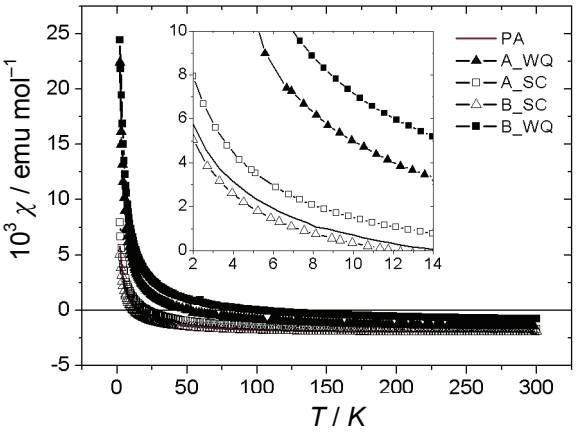

Figure 2. Magnetic susceptibility *versus* temperature measured in a magnetic field of H = 1 T. The inset shows a magnification for lower temperatures.

Table 1. The fitting parameters M_S and C, for the Brillouin[(a)] and Currie-Weiss[(b)] fit, respectively; the calculated mean effective Bohr magneton number per Mn atom, $\overline{p}_{\text{eff}}$, and the normalized mean effective magnetic moment per Mn atom, m. The value of C is given per mol of Mn atoms

Sample	M_S (emu/mol)	C (emu K/mol)	$\overline{p}_{\text{eff}}$	m
PA	46	4.1×10^{-3}	0.18	3.1×10^{-2}
A_WQ	287	8.8×10^{-3}	0.26	4.5×10^{-2}
A_SC	38	3.4×10^{-3}	0.17	2.8×10^{-2}
B_SC	58	5.0×10^{-3}	0.20	3.4×10^{-2}
B_WQ	371	11.6×10^{-3}	0.31	5.2×10^{-2}

[(a)] Eq. (1). [(b)] Eq. (2)

with different cooling rates, either SC at 10 K/h or abrupt cooling by WQ. We denoted the samples after additional thermal annealing by SAMPLE NAME_COOLING RATE (*i.e.* A_WQ).

Sample A was first annealed for 2 h and then WQ. Its normalized moment was determined to be $m_{\text{A\_WQ}} = 4.5 \times 10^{-2}$, which is significantly higher than the moment of sample PA. Next, sample A was additionally annealed for 45 h and then SC. Its normalized moment decreased to $m_{\text{A\_SC}} = 2.8 \times 10^{-2}$ which is similar to the value of the PA sample.

In the case of sample B the cooling rates were reversed with respect to sample A. First, sample B was subjected to thermal annealing lasting 2 h and then SC to room temperature. The normalized moment was found to be $m_{\text{B\_SC}} = 3.4 \times 10^{-2}$ which differs only a little from the value for sample PA. A considerable increase in the normalized moment was measured after additional annealing for only 5 min followed by WQ. The obtained value was $m_{\text{B\_WQ}} = 5.2 \times 10^{-2}$.

The above results are a clear evidence for the importance of the cooling rate after thermal annealing. As higher magnetizations are obtained in samples with a more disordered structure, magnetization measurements can be directly connected to the structural order of the sample.[1,2,3] By employing SC after thermal annealing, the sample does not change its magnetization significantly in comparison to the preannealed sample, suggesting that there was no considerable change in the degree of structural order. Thermal annealing followed by WQ, however, increases the magnetization of the sample despite the thermal history of the sample and thus introduces some disorder into the crystal structure.

The preannealing for 3640 h at 800 °C was long enough for thermal vacancies reaching equilibrium which means that the vacancies aggregate into large voids having diameters of 100–300 μm[4] and thus not dissolute in the material. All subsequent thermal treatments were too short to influence the vacancy concentration any further. In addition, there are no *T*-phase precipitates present in the material annealed at the temperature of 800 °C.[7] The only contribution to the short-scale disorder can thus be the contribution of thermal strains arising from strong temperature gradients caused by rapid cooling.

CONCLUSIONS

Applying WQ after thermal annealing causes strong temperature gradients resulting in the appearance of thermal strains in the crystal structure which can be detected indirectly by magnetic measurements. The magnitude of the electronic magnetization of the same *i*-Al-Pd-Mn material subjected to different cooling rates after thermal annealing varies to a factor of 1.7. The sample was properly preannealed so that we could exclude the influence of thermal vacancies and secondary phase precipitates on the magnetic properties.

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SAŽETAK

Utjecaj termičke obrade na strukturni red u *i*-Al-Pd-Mn kvazikristalima

Marko Jagodič,[a] Zvonko Jagličić,[a,b] Benjamin Grushko[c] i Janez Dolinšek[d]

[a]*Institute of Mathematics, Physics and Mechanics, Jadranska 19, SI-1000 Ljubljana, Slovenia*
[b]*Faculty of Civil and Geodetic Engineering, University of Ljubljana, Jamova 2, SI-1000 Ljubljana, Slovenia*
[c]*Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany*
[d]*Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia*

Ispitan je utjecaj brzine hlađenja na termičke deformacije u kvazikristalnim ikozaedarskim Al-Pd-Mn kompleksnim metalnim slitinama. Općenito je moguće, budući da su magnetski momenti Mn čvorišta jako ovisni o lokalnom okruženju, mjerenja elektronske magnetizacije koristiti kao posrednu metodu za određivanje kratkodosežnog nereda u kristalnoj strukturi. Isključujući, odgovarajućim odabirom temperatura i vremena preaniliranja, doprinose termičkih vakancija i precipitata druge faze moguće je promjene magnetizacije pripisati nastanku ili nestajanju termalnih deformacije u kristalnoj strukturi. Nađeno je da kaljenje u vodi povećava termalne deformacija neovisno o termičkoj povijesti.