

Investigation of Nanocrystalline Materials by PAC

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Abstract

The local sensitivity of perturbed $\gamma\gamma$ angular correlation spectroscopy (PAC) on an atomic scale is used for the investigation of nanocrystalline materials. In nanocrystalline Si and W, diffusion of the probe atoms ^{111}In via grain boundaries already occurs at temperatures of 850 K and 650 K, respectively. In the nanocomposite WGa two different local structures are detected via their characteristic EFG. The effect of mechanical alloying during ball milling is studied at the system $\text{Ti}_{1-x}\text{Al}_x$ ($x=0.5$). The observed EFGs are compared with those in the intermetallic compounds TiAl and Ti_3Al , prepared from the melt.

Introduction

During the last years, a new class of substances in the form of nanocrystalline materials was developed, which are, in principle, polycrystalline, but their crystallites are in the range of 10 nanometers [1]. This constitution results in properties that differ from those of conventional polycrystals or single crystals, such as altered mechanical behaviour, new magnetic features and, in the case of semiconductors, new optical properties. Another property consists in the possibility of forming compounds between materials that are immiscible under conventional conditions, such as W and Ga.

In this paper, results of perturbed $\gamma\gamma$ angular correlation (PAC) experiments are presented, which are aimed at a microscopic understanding of nanocrystalline materials via the use of radioactive probe atoms. In a first attempt, nanocrystalline metals and semiconductors, elemental systems and compounds were investigated, which were prepared by different techniques. PAC spectroscopy was already applied to the investigation of nanocrystalline materials, e.g. by P. Sinha and G. Collins [2].

Experimental details

PAC spectroscopy was performed using radioactive ^{111}In atoms and the microscopic information was deduced from the measured electric field gradient (EFG) that is typical for the environment of the probe nucleus within the sample material. The EFG is characterized by the coupling constant $\nu_Q = eQV_{zz}/h$, being proportional to the largest component V_{zz} of the EFG tensor in its principle axis system, and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ [3]. The values for ν_Q and η , presented in this paper, correspond to the values measured at 77 K.

Nanocrystalline W, Si and WGa samples were prepared by inert gas condensation. Here, the respective source material is evaporated or sputtered into an inert gas atmosphere of about a few millibars [1]. In this way, a condensation of nanometer-sized crystallites is effected, which condense on a cold-finger and are subsequently compacted into pellets. In the case of WGa, the components W and Ga were sputtered and evaporated, simultaneously. The WGa pellets, which are subject of this investigation, have a Ga content of 50 at% or 33 at%. The ^{111}In probe atoms were incorporated into the samples *ex-situ* by diffusion at 650 K (W), 850 K (Si) or 700 K (WGa).

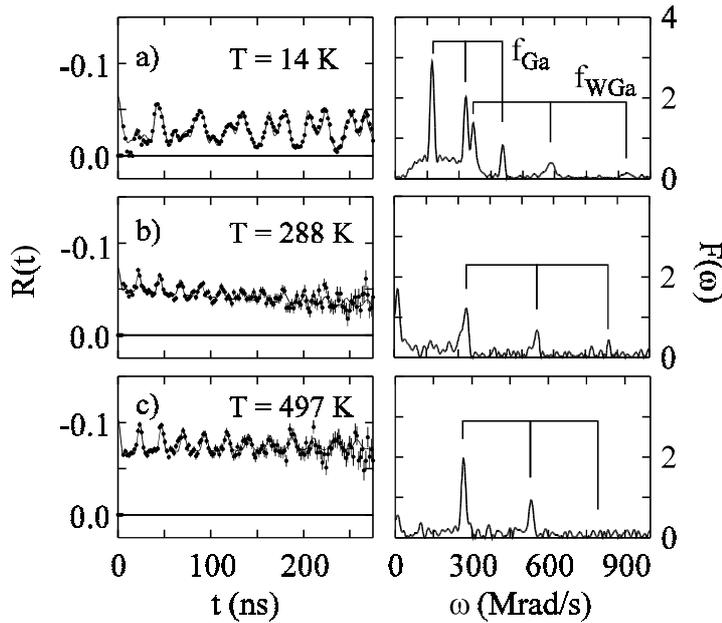


Fig. 1 : PAC spectra of WGa (50 at%) samples diffused with ¹¹¹In and measured at different temperatures *T*.

boundaries of these materials. There is no change in the PAC spectra observable after heating the samples at temperatures up to 1200 K. More detailed information was obtained from PAC experiments in WGa and TiAl :

WGa

The PAC spectra of a WGa sample (50 at% Ga) are shown in fig. 1, measured at different sample temperatures. At 14 K (fig. 1a), two EFGs are observed. The first one, designated by f_{Ga} , is characterized by $\nu_Q = 147$ MHz and $\eta = 0.2$ and corresponds to orthorhombic α -Ga [4]. The second EFG with $\nu_Q = 320$ MHz is axially symmetric and is neither known for pure W nor for pure Ga. This EFG, designated by f_{WGa} , is obviously typical for WGa and is visible up to at least 500 K, whereas the fraction f_{Ga} vanishes near room temperature, as expected due to melting of the Ga crystallites.

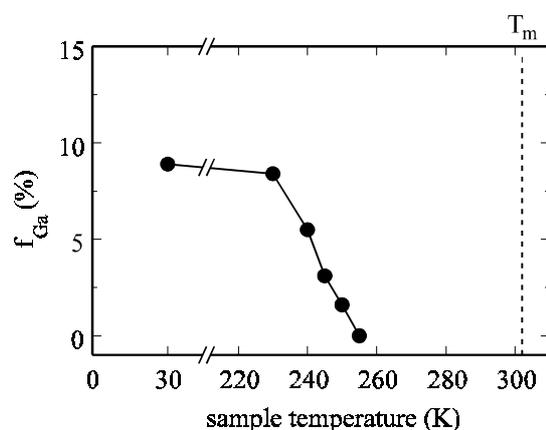


Fig. 2 : The fraction f_{Ga} of ¹¹¹In atoms as a function of sample temperature in the composite WGa (33 at% Ga).

Ti and Al foils were molten together in vacuum using an electron gun, in order to form $Ti_{1-x}Al_x$ compounds. For comparison, small pieces of Ti and Al were mechanically alloyed by ball milling for 24 h. All TiAl samples were doped with ¹¹¹In by diffusion at 910 K for 16 h under vacuum.

Results and discussion

In contrast to coarse grained material, in nanocrystalline W and Si, the diffusion of ¹¹¹In into the samples occurred already at such low temperatures as 650 K and 850 K, respectively. The PAC spectra show no well-defined EFG. In both cases, rather a broad distribution of EFGs, corresponding to non equivalent In sites, is observed. It is concluded that diffusion and incorporation of the ¹¹¹In probes takes place via the grain

A more detailed investigation of the melting behaviour of the α -Ga phase for a sample with 33 at% Ga shows a significant depression of the melting temperature from $T_m = 302$ K (bulk) to 240 K (fig. 2). In addition, it is evident that the melting process does not happen stepwise at a unique temperature, but occurs over a temperature interval of about 20 K. The shift of the melting

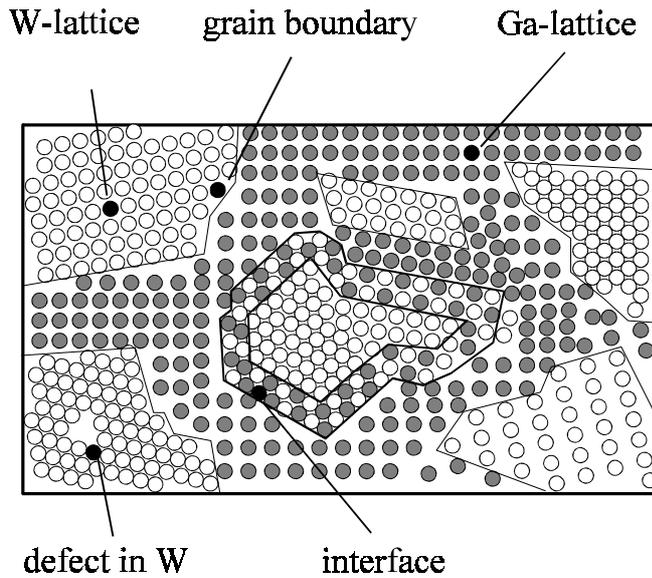


Fig. 3 : Microscopic model for the composite WGa consisting of W (open circles) and Ga atoms (grey circles). Possible sites for the incorporation of ¹¹¹In (closed circles) are indicated.

temperature is attributed to the small particle size [5] and the finite temperature interval is explained by the size distribution of the Ga crystallites.

In contrast, the local structure causing the EFG that corresponds to f_{WGa} is not yet identified. A schematic model of the composite WGa, as it is expected after the thermal treatment at 700 K, is shown in fig. 3. It consists of nanocrystalline W crystallites that are embedded in Ga. The Ga covers the W particles, thereby forming orthorhombic Ga crystallites (f_{Ga}).

Besides the Ga lattice, possible sites for the probe atoms are shown, which might explain the occurrence of the fraction f_{WGa} . An incorporation into the W lattice is not a likely explanation of the EFG, characterized by $\nu_Q = 320$ MHz, because the experiments at nanocrystalline W showed no incorporation of In on regular lattice sites at these temperatures and the incorporation at W grain boundaries was characterized by a frequency distribution rather than by a sharp frequency [6]. Although different defects in W were observed by PAC in the past [7,8], the observed EFGs do not correspond to that of f_{WGa} . Thus, a possible structure giving rise to this EFG might consist of an ordered arrangement of W and Ga atoms at the interface between both constituents. In order to examine this hypothesis, experiments at W-Ga interfaces, e.g. in W-Ga multilayers, will be performed.

Tab. 1 : Nanocrystalline materials investigated by PAC. The chosen preparation conditions and the observed EFGs are listed.

SAMPLE	W	Si	WGa	TiAl
production	inert gas condensation	inert gas condensation	inert gas condensation	ball milling
¹¹¹ In incorporation	diffusion	diffusion	diffusion	diffusion
EFG	no well-defined EFG	no well-defined EFG	147 MHz, $\eta=0.2$ 320 MHz, $\eta=0$	142 MHz, $\eta=0$ 268 MHz, $\eta=0$

TiAl

Most of the ¹¹¹In probe atoms in the TiAl samples, prepared by ball milling, are incorporated at non equivalent sites, which give rise to a frequency distribution in the range 100 MHz to 500 MHz (fig. 4a). Additionally, 10 % of ¹¹¹In probes are exposed to two well-defined, axially

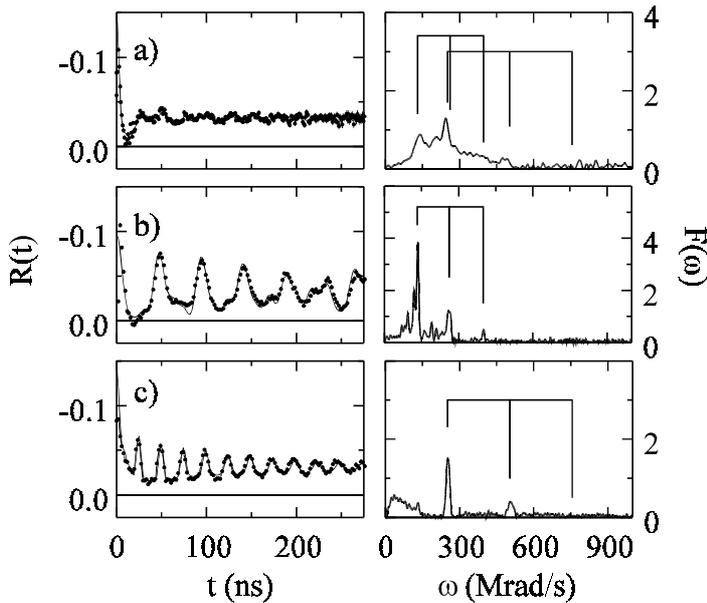


Fig. 4 : PAC spectra of $Ti_{1-x}Al_x$ samples. The spectrum of the mechanically alloyed sample (a) is compared with those of $TiAl$ (b) and Ti_3Al (c).

alloying process. The frequency distribution of the mechanically alloyed sample could be due to the fact that the In atoms are incorporated at non regular sites, which arise from amorphous structures induced by ball milling [10].

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symmetric EFGs, characterized by $\nu_{Q1} = 142$ MHz and $\nu_{Q2} = 268$ MHz. These two EFGs are also observed in $Ti_{1-x}Al_x$ reference samples, which were prepared from the melt. The dominant EFG of the stoichiometric intermetallic compound γ -TiAl with $x = 0.54$ (fig. 4 b) corresponds to $\nu_{Q1} = 142$ MHz and $\eta = 0$. It is attributed to the lattice field gradient of an ordered tetragonal $L1_0$ structure [9]. A sample with the composition $x = 0.33$ forms the intermetallic compound Ti_3Al with an ordered hexagonal $D0_{19}$ structure. The corresponding PAC spectrum (fig. 4c) is governed by a damped modulation with $\nu_{Q2} = 268$ MHz and $\eta = 0$. In this respect, mechanical alloying along with a subsequent heat treatment at 910 K needed for the diffusion of In, seems to produce different intermetallic compounds, thereby yielding the same local structures as a conventional