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PAC INVESTIGATIONS ON NANOSTRUCTURED MATERIALS

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Abstract - Because of its high local sensitivity the perturbed angular correlation spectroscopy (PAC) is well suited to study the local environment of radioactive probe atoms. In this way, the behaviour of probe atoms at interfaces, the influence of different preparation conditions on the formation of defect complexes, and the incorporation of impurity atoms is investigated whereby the probe atoms form either a constituent of the matrix or act as dopant atoms. First results of nanocrystalline WGa and CdS doped with the radioactive probe ^{111}In are presented.

Introduction

The properties of nanostructured materials are mainly determined by the size of the crystallites as well as by the interconnecting grain boundaries and defect structures and, therefore, are evidently different from those of polycrystals of the same chemical composition. Moreover, composites like FeAg or WGa, being immiscible under conventional conditions, can be formed if special techniques producing nanocrystalline materials are used, like inert gas condensation (1). While the technology for manufacturing nanocrystals has been developed to some extent, a fundamental understanding of the special properties of these materials is mostly lacking (2). Here, locally sensitive experimental techniques like Mössbauer spectroscopy, EXAFS or perturbed $\gamma\gamma$ -angular correlation (PAC) might be helpful for getting more information about grain boundaries, interfaces and defects within the formed crystallites. In addition, semiconductors of reduced dimensionality possess size dependent linear and non-linear optical properties and, therefore, are interesting materials for producing new optical devices (3). The electrical and optical properties of CdS particles are changed if they are doped with acceptor or donor atoms. Using the donor In the effect of doping can be pursued by PAC spectroscopy if it is possible to incorporate the radioactive isotope ^{111}In into the CdS particles during precipitation. Therefore, the aim of the here presented experiments was the doping of CdS particles with radioactive ^{111}In during precipitation.

Experimental Details

The principles of the PAC spectroscopy are described e.g. by Wichert et al. (4). PAC mostly uses the radioactive probe atom ^{111}In which emits a $\gamma\gamma$ cascade following its decay to the isotope ^{111}Cd via electron capture. The spatial emission probability of these γ rays depends on the hyperfine interaction between the quadrupole moment Q of the intermediate $5/2$ level of the probe nucleus ^{111}Cd and the external electric field gradient (EFG) caused by the local arrangement of the neighbouring lattice atoms. Therefore, by recording the second γ quantum of the cascade with respect to the first one as a function of the elapsed time this hyperfine interaction becomes observable because it causes a characteristic modulation of the time

spectrum containing the three frequencies ω_1 , ω_2 , and $\omega_3 = \omega_1 + \omega_2$ for each EFG due to the threefold energy splitting of the 5/2 level. The amplitudes of the frequency triplet are determined by the fraction of probe atoms residing in the environment that is characterised by this EFG, the ratio ω_2/ω_1 yields the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ of the EFG-tensor, and the value ω_1 is proportional to the largest component V_{zz} describing the strength of the EFG which is usually expressed by the quadrupole coupling constant $\nu_Q = eQV_{zz}/h$.

Samples prepared by inert gas condensation and compacted into pellets after condensation can, in principle, be diffused with the radioactive probe atoms. But, the temperature needed for diffusion might cause a further growth of the grains constituting the composite so that properties due to the small size of the crystallites will be lost. Therefore, the doping of the samples during preparation of the nanocrystalline composites represents the better choice but is more complicated and, for this reason, will be the topic of a future project.

The doping of nanocrystalline samples, produced by precipitation as the decisive step of the Sol-Gel technique (3), can exclusively happen *in-situ* during preparation. The procedure is easier performed than doping of samples during inert gas condensation. But, there still exists the problem of finding a suited environment for precipitation which supports the incorporation of the radioactive probe atoms into the nanocrystalline particles.

Results and Discussions

Subject of the present investigations were nanocrystalline Si and WGa samples, which were produced by inert gas condensation and were doped with ^{111}In atoms *ex-situ* by diffusion, and nanocrystalline CdS and AgCl, which were produced by precipitation and were doped *in-situ* with ^{111}In atoms. While for Si and AgCl no satisfactory PAC results have been obtained, up to now, first results emerged from the studies of WGa and CdS. It should be noted, however, that the WGa sample was altered by the diffusion process and the sizes of the CdS particles could not be determined in these first experiments.

The composite WGa

WGa samples (40-50 at% Ga) were produced by inert gas condensation and subsequently compacted into a pellet of 8 mm diameter with a thickness of about 0.5 mm. From this pellet pieces of about 2mm^3 size were

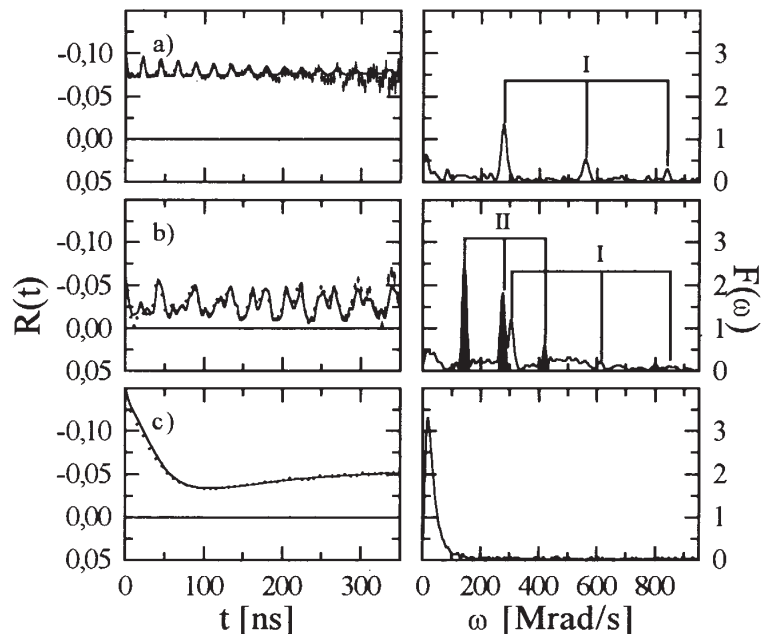


Fig. 1: PAC spectra taken at samples produced by inert gas condensation and diffused with ^{111}In : a;b) WGa measured at 295 K and 14 K, respectively, and c) W measured at 295 K

cut and at 700 K for 19 h diffused with the radioactive ^{111}In atoms from a dried solution of $^{111}\text{InCl}_3$. The EFG measured with the probe ^{111}In in $\alpha\text{-Ga}$ is known to be $\nu_Q = 142$ MHz with an asymmetry parameter of $\eta = 0.2$ (5), whereas in W some defect specific EFG are known after implantation of ^{111}In ions (6). The PAC spectrum in fig. 1a measured after diffusion shows a fraction of 17.5 % of the probe atoms within a well defined environment which is characterised by an axially symmetric EFG ($\eta = 0$) with the coupling constant $\nu_Q = 295$ MHz (I), that is not known from a defect in Ga or W. Upon cooling the sample to $T_m = 14$ K this EFG is shifted to 326 MHz (fig. 1b) and, additionally, the EFG known from $\alpha\text{-Ga}$ is observed proving the precipitation of Ga metal (II). At the same time a growth of the W particles occurs as determined by X-Ray scattering. Moreover, the structure characterised by the first EFG, was not observed in nanocrystalline W samples (fig. 1c) prepared in the same way as the composite WGa. The observed absence of the Ga specific EFG above 295 K is reversible and due to the melting of the precipitated Ga metal. This temperature indicates a depression of the melting temperature of Ga (302 K) within the composite WGa which will be investigated in future PAC experiments. The alteration of the melting point within nanocrystalline compounds is a general feature of this class of materials and most probably due to the dependence of thermal vibrations of the matrix atoms on the size of the crystallites (7). The origin of the structure characterised by the new EFG is not yet understood but, most probably, connected to an interaction between W and Ga atoms within the grain boundaries.

Precipitated CdS

The PAC results obtained for precipitated CdS are compared with those obtained on CdS bulk crystals thereby facilitating the identification of the observed local structures. A spectrum measured at highly In doped ($[\text{In}] = 10^{19} \text{ cm}^{-3}$) bulk CdS is plotted in fig. 2c and shows that 55 % of the In atoms reside in a defect structure characterised by an EFG with $\nu_Q = 125$ MHz and $\eta = 0.25$. The exact local structure of this defect is not yet identified but is strongly correlated to the high concentration of In atoms. The second fraction of In atoms, visible in fig. 2c, is located at unperturbed Cd sites which are characterised by an axially symmetric EFG with $\nu_Q = 7.5$ MHz resulting from the hexagonal lattice structure of CdS. The data known for highly In doped CdS single crystals are of special interest because in nanocrystalline CdS already a few In atoms effect a high In concentration: For

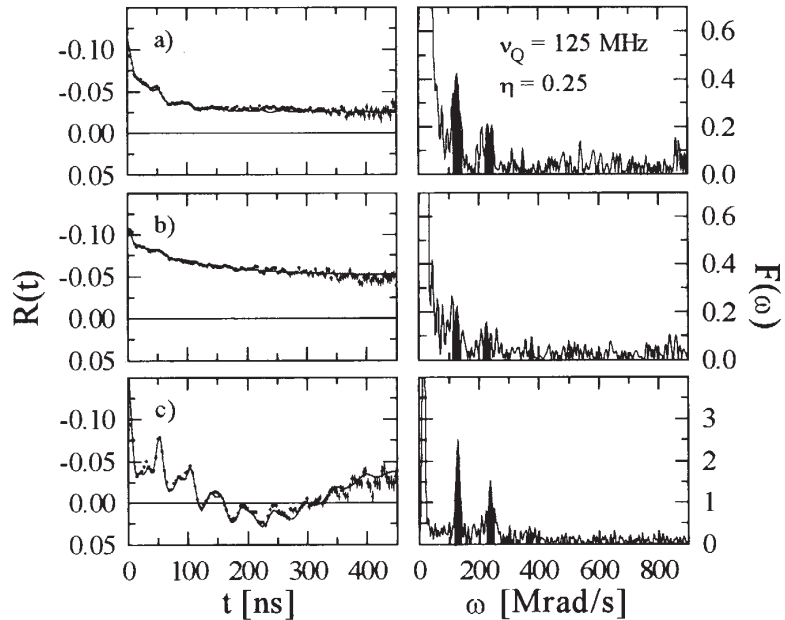


Fig. 2: PAC spectra taken at different ^{111}In doped CdS samples: a) precipitated in acetic acid, b) precipitated in ethanolic solution using HMDS, and c) highly In doped bulk crystal

example, one In atom within a CdS particle of 100 nm diameter corresponds to a concentration of about $5 \cdot 10^{16} \text{ cm}^{-3}$. The formation of nanocrystalline CdS via the Sol-Gel technique happens by precipitating CdS in an ethanolic solution of Cd ions by adding hexamethyldisilthiane (HMDS). HMDS reacts with ethanol and, thereby, produces H_2S reacting with the Cd ions to CdS. The size of the CdS particles was adjusted by adding different types of silane to the solution. Subsequently, the CdS particles were embedded into a network of ormocer (organic modified ceramics) or SiO_2 which is produced from the silanes forming a part of the solvents (3).

For precipitating CdS doped with ^{111}In , in a first experiment radioactive $^{111}\text{InCl}_3$ was added to a solution of CdCl_2 in acetic acid and subsequently H_2S gas was bubbled through this solution. The solution was removed by filtration, the residue washed with methanol and subsequently dried at a temperature of $T = 80 \text{ }^\circ\text{C}$. The measured radioactivity showed 60 % of the ^{111}In atoms to be within the residue. The PAC spectrum taken after this procedure (fig. 2a) established 4.5 % of the probe atoms to be within the same defect structure which is characterised by $\nu_Q = 125 \text{ MHz}$, $\eta = 0.25$ and is known from the highly In doped CdS bulk crystals. This result proves the incorporation of the In atoms into the precipitated CdS particles. A second fraction of In atoms (65 %) is most probably located at almost unperturbed Cd sites within the CdS lattice, what is indicated by the small slope at the beginning of the PAC spectrum. Using an ethanolic solution of Cd ions and precipitating CdS by adding of HMDS 30 % of the In atoms are found to be in the extracted residue whereby they are located within an undefined environment. After having precipitated CdS again out of the separated solution by a second addition of HMDS the PAC spectrum plotted in fig. 2b was obtained showing that now 3 % of the In atoms are located within the identical defect structure that is known from the highly In doped CdS bulk crystals. At the same time, about 30-40 % of the In atoms are located at Cd sites in CdS lattice as indicated by a broad EFG distribution around 5 MHz. These results clearly show the importance of purification of the solution in the first step of precipitation and the possibility of doping CdS particles with In atoms during precipitation.

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