Journal of Alloys and Compounds 552 (2013) 190–194

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

^{111}Cd-TDPAC study of pressure effect on the valence of Yb in the $YbGe_{2.85}$ cubic phase

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ARTICLE INFO

Article history:
Received 17 July 2012
Received in revised form 3 October 2012
Accepted 7 October 2012
Available online 13 October 2012

Keywords:
New phases
High pressure synthesis
Quadrupole frequency
Mixed valence
PAC method

ABSTRACT

New cubic phases of $YbGe_{2.85}$, $TbGe_{2.85}$ and $DyGe_{2.85}$ crystallized in the $AuCu_3$ structure are synthesized at a pressure of 8 GPa. Using the differential perturbed angular $\gamma\gamma$-correlation method (TDPAC) we measure the electric field gradient V_{zz} (the quadrupole frequency $\nu_Q = eQV_{ZZ}/h$) at ^{111}Cd nuclei probes inserted in Ge vacancy lattice sites for all these compounds. In $YbGe_{2.85}$ the electric field gradient (EFG) is obtained as a function of pressure (up to 8 GPa) at room temperature and as a function of temperature (down to 4 K) at normal pressure. In $TbGe_{2.85}$ and $DyGe_{2.85}$ EFG is measured only as a function of temperature (down to 77 K) at normal pressure. In $YbGe_{2.85}$ the change of EFG and ν_Q with pressure indicate a change of Yb valance from 2.46 at normal pressure to 2.89 at 8 GPa. In all compounds EFG and ν_Q are found to be practically independent of temperature.

1. Introduction

High pressure and temperature synthesis of superconducting Si and Ge-based clathrates of alkaline earths [1–4] has prompted much interest toward unusual physical properties of novel rare earth (RE) germanium compounds metastable at normal conditions. For example, the intermetallic compound $LaGe_5$ synthesized at 5 GPa was found to be a superconductor with the critical temperature T_c = 6.8 K [5]. It crystallized in the orthorhombic space group I/mmm ($Z = 2$) with the lattice constants $a = 4.0290(6)$, $b = 6.307(1)$, $c = 9.978(2)$ Å (the volume $V = 253.54(6)$ Å^3). The highest critical temperature among germanides, T_c = 7.4 K, was detected in $LaGe_3$ also synthesized at high pressure. It crystallizes in the $BaPb_3$ structure (the $R\bar{3}m$ space group) with the lattice constants $a = 6.376(1)$ Å, $c = 22.272(3)$ Å [6].

For the first time a cubic phase was reported in $CeGe_3$ at the pressure 5 GPa and the temperature 1900 K [7]. It has the $AuCu_3$ crystal lattice (the $Pm\bar{3}m$ space symmetry) with $a = 4.354(4)$ Å. The effective magnetic moment of this compound, 0.63 μ_B is appreciably smaller than the Ce^{3+} theoretical value of 2.54 μ_B. Another compound of this family, $YbGe_3$, was synthesized at pressures higher than 5 GPa and temperatures 1100–1400 K from the mixture of Ge with Yb_3Ge_8 [8]. It has the same $AuCu_3$ structure with the lattice constant $a = 4.276$ Å and displays a paramagnetic susceptibility. Interestingly, X-ray absorption spectroscopy (XAS) finds a fluctuating behavior of Yb ion valence with an average value of +2.4 [8].

On the other hand, it should be pointed out that at normal pressure $YbGe_{2.83}$ which is a germanium deficient material, crystallizes in another structure of trigonal symmetry (the $P\bar{3}m1$ space group) with the lattice constants $a = b = 8.3657(12)$ Å and $c = 7.0469(14)$ Å [9]. The structure of $YbGe_{2.83}$ is a variant of the $CaAl_2Si_2$ structure type with ordered vacancies. The deficiency at the Ge sites and the Zintl phase description of $YbGe_{2.83}$ suggest an overall mixed/intermediate valence for Yb ($Yb^{+2.35}$) [9].

Mixed valence ytterbium germanium binary compounds with stoichiometry close to 1(Yb):3(Ge) demonstrating complex behavior with pressure and temperature can be studied by the time-differential perturbed angular correlation method (TDPAC) of nuclear spectroscopy. Earlier this method was applied to study $YbAl_2$ where a linear dependence of the quadrupole frequency of probe nuclei on the valence of Yb ions caused by external pressure

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http://dx.doi.org/10.1016/j.jallcom.2012.10.025

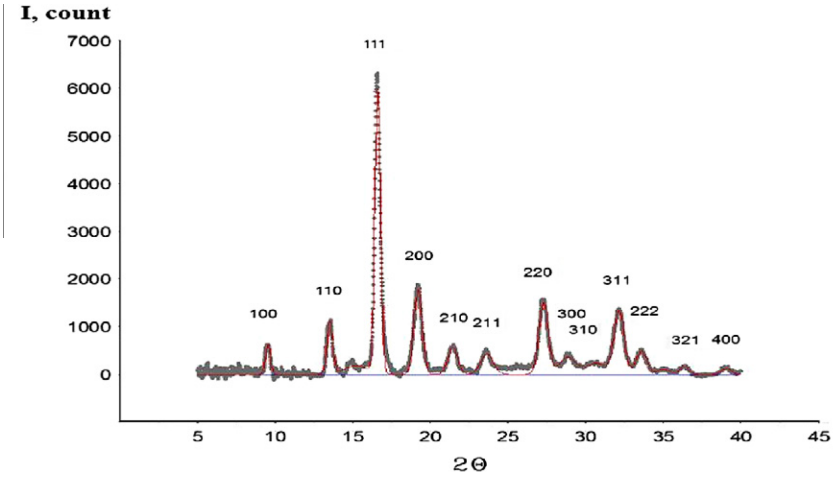

Fig. 1. X-ray powder diffraction pattern of $YbGe_{2.85}$ (the reflections which are not marked by indices *hkl* are from a NaCl container).

was established [10]. The effect of linear dependence of valence with pressure then has been used to determine the valence of Yb in other compounds.

In the present work we report on our TDPAC study of *cubic phases* of $YbGe_{2.85}$, $TbGe_{2.85}$ and $DyGe_{2.85}$, which are metastable at normal conditions. All these compounds are synthesized at high pressures and have germanium vacancies where probe $^{111}In/^{111}Cd$ isotopes are then inserted to measure the electric field gradient (or the quadrupole frequency). Germanium vacancies are found essential for TDPAC measurements because probe isotopes have tendency to avoid occupied germanium sites. (The problem is discussed in Ref. [15]). The focus of the present study is on $YbGe_{2.85}$ because Yb exhibits mixed valence behavior. For $YbGe_{2.85}$ we have measured quadrupole frequency on cooling down to 4 K at normal pressure and with increasing pressure to 8 GPa at room temperature.

2. Experiment

Polycrystalline samples of $YbGe_{2.85}$, $TbGe_{2.85}$, $DyGe_{2.85}$ and $EuGe_3$ were synthesized at a pressure of 8 GPa as described by Tsvyashchenko in Ref. [11].

Measurements were carried out by the TDPAC method using the 171–245 keV γ–γ cascade in ^{111}Cd populated through the 2.8 d isotope ^{111}In electron capture decay. The cascade proceeds via the 245 keV level with the half-life $T_{1/2} = 84$ ns, spin $I = 5/2$, and quadrupole moment $Q = 0.83$ b.

The ^{111}In activity was produced via the $^{109}Ag\,(\alpha,2n)\,^{111}In$ reaction through irradiating a silver foil with the 32 MeV α-beam. The ^{111}In–^{111}Cd nuclear probes were introduced into the lattice of $YbGe_{2.85}$, $TbGe_{2.85}$ and $DyGe_{2.85}$ by the high-pressure synthesis: the constituents (Yb, Tb, Dy and Ge) taken in proper amounts with an overall weight of about 500 mg were melted together with a small piece of the irradiated silver foil ($\approx$0.5 mg) in a special chamber under pressure of 8 GPa [12]. Powder X-ray diffraction (XRD) was performed at room temperature using a STOE IPDS-II diffractometer with Mo-Kα radiation and a graphite monochromator.

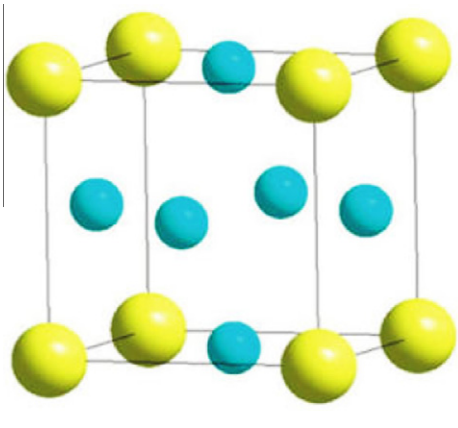

Fig. 2. Crystal lattice of the $YbGe_{2.85}$ cubic phase (the $AuCu_3$ structure). The Ge atoms (blue spheres) are smaller than the Yb atoms (yellow spheres). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

A 300 mg sample of $YbGe_{2.85}$ doped with ^{111}In was positioned inside a rock-salt ampoule that was used as a pressure-transmitting medium. The high pressure was generated in a calibrated "toroid"-type device [10].

The TDPAC pressure measurements were carried out using a four-detector spectrometer equipped with a small-size hydraulic four-arm press of the capacity upto 300 t [13].

For low temperature measurements the four-detector spectrometer was equipped with a four-window optical cryostat of the firm «JANIS» (modified model SHI-950).

As the samples were polycrystalline and paramagnetic at room temperature, the perturbation of the angular correlation can be described by the perturbation factor for the static electric quadrupole interaction [14]:

$$G_{22}(t;\nu_Q,\eta,\Lambda) = s_{20} + \sum s_{2n}\cos(\omega_n t)\exp(-1/2\Lambda\omega_n t)$$

Here the hyperfine frequencies ω_n ($n = 1, 2, 3$) depend on the quadrupole coupling constant $\nu_Q = eQV_{ZZ}/h$ called below the quadrupole frequency (QF) and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, where $V_{ii} = \partial^2 V/\partial i^2$ ($i = x, y, z$) are the principal-axis components of the electric field gradient tensor. The largest component proportional to ν_Q is the electric field gradient (EFG). The coefficients s_{2n} depend only on η ($1 \geqslant \eta \geqslant 0$). The exponential factor accounts for possible random lattice defects, while Λ is the relative half-width of the Lorentzian distribution. Here we restrict ourselves to the perturbation parameter of the second order since the unperturbed angular correlation coefficient $A_{44} \ll A_{22}$ ($A_{22} = -0.18$).

The perturbation factor $G_{22}(t)$ describing a nuclear spin precession due to a hyperfine interaction, was determined in a usual way from the angular anisotropy, obtained by combining the delayed coincidence spectra measured at the angles of 90^o and 180^o between detectors, $N(90^o,t)$ and $N(180^o,t)$, through the expression $R(t) = -A_{22}QG_{22}(t)$. Here

$$R(t) = 2[N(180^\circ,t) - N(90^\circ,t)]/[N(180^\circ,t) + 2N(90^\circ,t)],$$

is the solid-angle correction.

3. Results and discussion

First, we have performed the X-ray powder diffraction experiments for $YbGe_{2.85}$, $TbGe_{2.85}$ and $DyGe_{2.85}$. The $YbGe_{2.85}$ pattern is shown in Fig. 1. The study yields the $AuCu_3$ cubic structure with the $Pm\bar{3}m$ space group for all compounds. The lattice constants are $a = 4.274(4)$ Å, $a = 4.287(4)$ Å and $a = 4.286(4)$ Å for $YbGe_{2.85}$, $TbGe_{2.85}$ and $DyGe_{2.85}$, respectively.

The $AuCu_3$ structure (see Fig. 2) can be viewed as a framework of Ge_6 octahedra sharing corners with the large Yb atoms in the interstitials between octahedra. The Yb site has the cubic O_h site symmetry with zero electric field gradient. On the other hand, the Ge site has the D_{4h} site symmetry with a principal fourfold axis of symmetry. This site symmetry allows for a quadrupole electric