Charge segregation in Yb₄As₃ observed using $^{172}$Yb PAC probe

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We present results of PAC measurements in heavy-fermion compound Yb₄As₃. The quadrupole hyperfine interaction has been investigated over the temperature range 78–850 K. The interpretation of the experimental data yields a microscopic proof of the existence of a charge-ordered state with periodic arrangement of Yb²⁺ and Yb³⁺ ions in the low temperature phase. In the high temperature phase all Yb ions are in a valence fluctuating state.

1. Introduction

The rare-earth compound Yb₄As₃ shows unusual physical properties. This semiconductor has a structural phase transition at about $T_0 = 295$ K. In the low temperature phase it behaves like a heavy-fermion compound [1]. Specific heat measurements give a large linear specific heat coefficient $\gamma$ of about 200 mJ/mol K² and the resistivity shows a $T^2$ variation up to 50 K. The Wilson ratio and the value $A/\gamma^2$ (where $A$ is the $T^2$ coefficient of the resistivity) correspond to the Fermi-liquid behaviour. An unusual feature is an extremely low carrier concentration derived from the Hall coefficient measurements. With the charge carrier density of 0.001 per Yb³⁺ ion, Yb₄As₃ cannot be classified as a normal Kondo system, where a substantial amount of conduction electrons is thought to be necessary to develop a singlet state.

Above room temperature Yb₄As₃ has the cubic anti-Th₃P₄ type structure (space group I43d) with $a = 8.789$ Å and the free parameter $u = 0.069(1)$ [2]. All 16 Yb atoms in the unit cell are in equivalent positions on a three-fold symmetry axis. Below $T_0$ the crystal shrinks along the $\langle111\rangle$ direction to the R3c rhombohedral structure with almost the same lattice constant and $\alpha = 90.8^\circ$, whereas the atomic positions in the unit cell remain unchanged. After such deformation 4 Yb positions remain on a three-fold axis along the $\langle111\rangle$ direction, while the rest of 12 locations have no such symmetry.
It is believed that a small lattice distortion at the phase transition point is accompanied by a charge ordering of Yb\(^{2+}\) and Yb\(^{3+}\) ions. This hypothesis comes from magnetic susceptibility measurements. In the range 80–295 K, the \(1/\chi\) versus \(T\) dependence can be reproduced assuming the ratio of Yb\(^{2+}\) and Yb\(^{3+}\) ions being 3 : 1 (Yb\(^{3+}\) ion has 4f\(^{13}\) configuration with \(J = 7/2\) and is paramagnetic, while Yb\(^{2+}\) with 4f\(^{14}\) ground state and \(J = 0\) is diamagnetic). A microscopic Mössbauer effect measurement confirmed the existence of two types of Yb ions at low temperatures [3]. However, both the susceptibility and Mössbauer effect experiments leave an open question whether Yb\(^{3+}\) ions create their own regular sublattice or di- and trivalent ions are randomly scattered over Yb positions in the crystal lattice. As a matter of fact the structural deformation suggests that Yb\(^{3+}\) ions with smaller atomic radii than Yb\(^{2+}\) occupy positions along the ⟨111⟩ axis. On the other hand, no magnetic ordering was observed down to 0.045 K, which may indicate that magnetic ions could be scattered at random positions in the lattice [3].

The perturbed angular correlation (PAC) technique offers another possibility to perform a microscopic study of Yb\(_4\)As\(_3\). Applying an \(^{172}\)Yb probe, which is the daughter nucleus of radioactive \(^{172}\)Lu, one expects to distinguish the valence states of Yb ions through the quadrupole hyperfine interaction. Contrary to Mössbauer spectroscopy, an important advantage of the PAC technique is its constant efficiency in a broad range of temperature. Thus, the microscopic measurements can also be performed for the high temperature phase of Yb\(_4\)As\(_3\).

2. Sample preparation and experiment

The procedure of the Yb\(_4\)As\(_3\) compound synthesis is described in ref.[1]. About 100 mg of Yb\(_4\)As\(_3\) powder was irradiated with 14 MeV deuterons at the Krakow cyclotron. The radioactive \(^{172}\)Lu \((T_{1/2} = 6.7\) d\) was produced in the target as a result of the \(^{172}\)Yb (d, 2n) \(^{172}\)Lu and \(^{171}\)Yb (d, n) \(^{172}\)Lu nuclear reactions. In a period from 2 days till 3 weeks after the irradiation the \(^{172}\)Lu activity was dominating in the radioactive source. A suitable piece of the target material, containing about 5 \(\mu\)Ci of \(^{172}\)Lu was sealed in a quartz tube in vacuum and then mounted in a \(\gamma\)–\(\gamma\) angular correlation apparatus.

The radioactive decay of \(^{172}\)Lu is rather complex and contains over 100 \(\gamma\) transitions. A partial decay scheme is shown in fig. 1. It presents the level of interest, namely the 1172 keV excited level of \(^{172}\)Yb with \(I = 3\) and \(T_{1/2} = 8.3\) ns, and all \(\gamma\) transitions which populate or deexcitate from it. Several \(\gamma\)–\(\gamma\) cascades may be selected. The most favorable characteristics are for the 91–1094 keV cascade with the relatively large anisotropy coefficient \(A_2 = +0.28\) and reasonable line intensities of 7 and 97%, respectively.

The PAC data were taken with a four-detector setup equipped with BaF\(_2\) detectors. The time resolution of the system was found to be about 550 ps. Two detectors with 3 mm thin scintillators were assigned for detection of the 91 keV radiation.