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In-beam Mössbauer spectroscopy of ^{57}Mn implanted into lithium hydride

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Abstract We measured the temperature dependence of ^{57}Fe Mössbauer spectra obtained after ^{57}Mn implantation into polycrystalline LiH with an extremely low implantation dose. Density functional calculations suggested that the Fe atoms were predominantly implanted into both Li and H substitutional sites of the LiH crystal.

Keywords ^{57}Fe Mössbauer spectroscopy · Radioactive ^{57}Mn beam · LiH

1 Introduction

In-beam Mössbauer spectroscopy based on ^{57}Fe arising from short-lived ^{57}Mn ($T_{1/2} = 87.2$ s) can provide direct information on the electromagnetic properties

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of the surrounding environment and on exotic oxidation states and novel chemical bondings of unstable nuclear probes such as ^{57}Mn/^{57}Fe implanted into $KMnO_4$ [1] and O_2 solids [2]. Recently, our detection system was successfully improved to obtain ^{57}Mn/^{57}Fe in-beam Mössbauer spectra with a very high signal/noise ratio at the Heavy Ion Medical Accelerator in Chiba (HIMAC) facility of the National Institute of Radiological Sciences NIRS [3]. We applied this improved detection system to investigations of ^{57}Mn/^{57}Fe in metal oxides [4] and rock salt type crystals, e.g. alkali halides and lithium hydride (LiH). The crystal structure of LiH contains one Li^+ cation surrounded by six H^- anions. A stable ternary compound Mg_2FeH_6 consisting of $[FeH_6]^{4-}$ complex anion has been reported [5], but binary compounds of hydrogen and iron or manganese have not been synthesized. In the present work, we investigated the chemical and physical behaviors of ^{57}Fe arising from ^{57}Mn in LiH.

2 Experiment

The experiment was carried out at the heavy ion synchrotron facility HIMAC of NIRS [6]. The basic experimental setup was described previously [3, 4]. Radioactive ^{57}Mn ions were used as a highly energetic secondary beam ($E =\sim 260A$ MeV) which was produced from the projectile fragmentation process of nuclear collisions between ^{58}Fe ions ($500A$ MeV, $\sim 1 \times 10^8$ particles per beam) and ^{9}Be nuclei in a 27-mm-thick production target. The ^{57}Mn beam was purified by a fragment separator installed in the secondary beam line SB2 of the HIMAC facility, and the purity was higher than 80%. The typical implantation dose of ^{57}Mn was about 1×10^6 particles per beam. The period of the ^{57}Mn secondary beam was active for $\sim$ 300 ms every 3.3 s. The implantation depth of the ^{57}Mn ions was controlled by passing the ion beam through an appropriate combination of energy degraders. LiH powder, purchased from Wako Pure Chemical Industries, was used to cover a 33 × 33 mm area to a depth of about 3 mm, which was sufficient to stop all of the ^{57}Mn ions within the sample. The LiH sample was mounted on a boron nitride heater in a vacuum chamber in order to control the sample temperature in the range from room temperature to over 800 K. After β decay of the implanted ^{57}Mn, the 14.4-keV γ rays emitted from ^{57}Fe were selectively detected by a combination of a Mössbauer resonance counter (parallel plate avalanche counter—PPAC) [7] and an anti-coincidence method to reject the β rays [3]. The PPAC was mounted on the Mössbauer driving unit to apply the Doppler velocity. Using this new detection system, we were able to obtain emission Mössbauer spectra of high quality using a very small number of implanted ^{57}Mn ions, realizing an environment in which each implanted ^{57}Fe atom is completely isolated from the other ^{57}Fe atoms in the sample.

3 Results and discussion

Mössbauer spectra of ^{57}Mn/^{57}Fe in LiH at room temperature and at 623 K were obtained, as shown in Fig. 1 together with several best-fit singlet and doublet curves, assuming a Lorentzian shape. Figure 1 suggests that with increasing sample temperature, the symmetrical crystalline structure surrounding the Fe atom was recovered

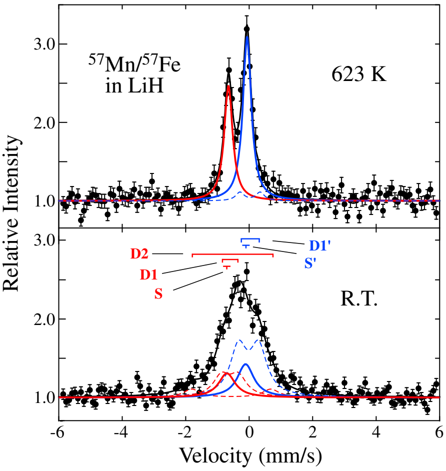

Fig. 1 Obtained emission Mössbauer spectra of ^{57}Fe after β decay of ^{57}Mn implanted into LiH along with best-fit curves. The *red* and *blue lines* correspond to Fe atoms that substitute Li and H sites, respectively, according to estimations based on density functional calculations. For more details, see the text

Table 1 Emission Mössbauer parameters of ^{57}Mn implanted into LiH

	^{57}Fe at Li substitutional site				
	Experimental		Theoretical		
	$I.S.$ (mm/s)	$\lvert\Delta E_Q\rvert$ (mm/s)	$I.S.$ (mm/s)	ΔE_Q (mm/s)	
S	−0.76(6)	–	−0.558	–	
D1	−0.63(9)	0.56(6)	−0.577	0.463	(with a Li defect)
D2	−0.60(28)	2.41(54)	−0.705	−2.091	(with a H defect)
	^{57}Fe at H substitutional site				
	Experimental		Theoretical		
	$I.S.$ (mm/s)	$\lvert\Delta E_Q\rvert$ (mm/s)	$I.S.$ (mm/s)	ΔE_Q (mm/s)	
S’	−0.19(5)	–	−0.015	–	
D1’	−0.04(5)	0.69(11)	−0.105	−0.534	(with a Li defect)
			−0.105	−0.533	(with a H defect)

The sign of isomer shift $I.S.$ in the obtained emission Mössbauer spectrum was opposite to that of conventional absorption Mössbauer spectrum

by an annealing effect. The Mössbauer spectrum obtained at 623 K indicated that two singlets S and S’ were dominant, and the isomer shifts ($I.S.$) were determined to be −0.76(6) mm/s and −0.19(5) mm/s, respectively, relative to Fe metal at room temperature.

Density functional calculations were performed for an Fe atom surrounded by a Li_mH_n lattice with an additional 412 point charges (±1) to predict the Mössbauer parameters. For the Li substitutional site ($m = 42$ and $n = 38$), the isomer shift was estimated to be $I.S. = -0.588$ mm/s, and $I.S. = -0.015$ mm/s for the H substitutional site ($m = 38$ and $n = 42$). Comparing the observed spectra to these predictions suggests that the Fe atom was located at a Li substitutional site for the singlet S and at an H substitutional site for the singlet S’. The doublet D1 (D2) in Fig. 1 corresponds to an Fe atom at a Li substitutional site with a missing nearest Li(H) atom. D1' corresponded to an Fe atom located at an H substitutional site with a neighboring Li or H defect. These Mössbauer parameters are summarized in Table 1. To confirm the implantation sites and to discuss the more detailed chemical states, systematic measurements at the temperature range from 10 to 800 K and additional numerical analysis are underway.

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