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In-beam Mössbauer study of ^{57}Mn implanted into a low-temperature xenon

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Abstract The in-beam Mössbauer spectrum of ^{57}Mn implanted into a Xe solid at 14 K was measured. Four singlets were observed in the spectrum, assigned to $^{57}Fe^{+}$ ($3d^7$), $^{57}Fe^{+}$ ($3d^6 4s^1$), $^{57}Fe^0$ ($3d^6 4s^2$), and $^{57}Fe^0$ ($3d^7 4s^1$). The assignments were in agreement with calculated electron densities at nuclei reported in the literature.

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The β-decay of ^{57}Mn did not disturb the surrounding Xe lattice, showing a singlet peak, and the excited states were stabilized in the time range of the Mössbauer measurements of ~100 ns. The production mechanism was explained in terms of the reduction of $^{57}Mn^{x+}$ and $^{57}Fe^{y+}$ ions by free electrons in the Xe matrix.

Keywords In-beam Mössbauer spectroscopy · ^{57}Mn · ^{57}Fe · Electronic configuration · Xe solid

1 Introduction

In-beam Mössbauer spectra of ^{57}Mn provide useful information on the surrounding solid material. ^{57}Mn has a short lifetime (126 s); hence, the Mössbauer spectra have to be measured using an in-beam setup combined with a heavy-ion accelerator. This technique has been applied to probe the nature of metal oxides [1] and metal halides [2]. Studies using ^{57}Mn are also important for providing a new source material for chemical reactions, as the after-effects of β-decay are generally small. It has been reported that β-decay of ^{57}Mn produced ^{57}Fe with increased valence without disturbing the surrounding materials or the chemical structure [3]. ^{57}Mn implanted into rare gas solids represents the simplest system to study the chemical and electronic states of ^{57}Fe atoms produced just after the β-decay of the parent ^{57}Mn.

The matrix isolation technique is useful for studying unstable species by trapping them in an inert matrix. Mössbauer spectra of Fe atoms in an Ar matrix have been reported by Barrett [4], and Fe atoms and Fe_2 dimers were found. Emission Mössbauer spectra of ^{57}Co in low-temperature Xe matrices have been reported by Micklitz [5], and Fe^+ and Fe^0 were found as produced after a nuclear electron-capture (EC) decay of ^{57}Co. The implantation of ^{57}Co into solid Ar was performed in a very clean system [6, 7], and two kinds of electronic configurations, $3d^7$ and $3d^64s^1$, were found for Fe^+. The production mechanism of Fe^+ with the excited electronic $3d^7$ state was explained in terms of charge transfer between the ^{57}Fe atom and surrounding Ar atoms [8] as well as the insulating nature of Ar. EC decay of ^{57}Co produced defects in the fcc Ar lattice, which allowed for the transition from $3d^7$ to $3d^64s^1$.

We have previously reported the in-beam Mössbauer spectra of ^{57}Mn implanted into a low-temperature Ar matrix, where the the spectra were measured during implantation into Ar at 18 K [9]. Only one singlet peak ($\delta = -2.16(2)$ mm/s) assigned to $^{57}Fe^+$ ($3d^7$) was found, indicating that the ^{57}Fe atoms produced by β-decay of ^{57}Mn had a unique form, and were not a mixture of the ground state $^{57}Fe^+$ ($3d^64s$) or neutral $^{57}Fe^0$. It was explained that the $^{57}Mn^{2+}$ ion was trapped in a substitutional position of the fcc Ar lattice, and that $^{57}Fe^{3+}$ was produced by β-decay of ^{57}Mn without disturbing the surrounding Ar lattice, which was followed by a charge transfer process with neighboring Ar resulting in the production of $^{57}Fe^+$ ($3d^7$).

In this study, we investigated the in-beam Mössbauer spectrum of ^{57}Mn implanted into a low-temperature Xe matrix. The nature of a Xe solid is different from that of an Ar solid. The electron mobility of an Ar solid and Xe solid are reported to be 1000 and ~4500 $cm^2V^{-1}s^{-1}$, respectively [10]. The combination with free electrons is more dominant in the Xe matrix, and the emission Mössbauer spectra of ^{57}Co in the

Xe matrix showed both Fe^+ ($3d^7$) and Fe^0 ($3d^64s^2$) [5, 11]. It is interesting to study the fate of ^{57}Fe produced by the β-decay of ^{57}Mn in the Xe solid in which free electrons are not negligible, and Fe atoms or ions with different electronic configurations other than Fe^+ ($3d^7$) may be obtained in the Xe matrix.

2 Experimental

The measurements were performed at the National Institute of Radiological Sciences (NIRS) in Chiba, Japan, using a heavy-ion synchrotron accelerator (HIMAC). A projectile fragmentation reaction of a primary beam of ^{58}Fe ions and a target of ^{9}Be atoms produced the ^{57}Mn nuclei. A beam pulse of 1.2×10^6 particles was generated every 3.3 s with a 250 ms duration. A parallel-plate avalanche counter (PPAC) [12] was employed as a detector. The anti-coincidence method was employed to obtain high-quality spectra with improved S/N ratios [13]. Xe solid samples were prepared on a substrate made of brass cooled down to 14 K using a pulsed tube refrigerator. Xe gas with purity of 99.999 % was introduced at 1.50 sccm (standard cubic centimeters per minute) using a flow controller for 49 h; the Xe solid had a thickness of approximately 3 mm. The implanted ^{57}Mn atoms were distributed around a depth of 0.1 mm from the surface of the Xe solid. The measurement was performed for 42 h while implanting ^{57}Mn. The mixture ratio of the atoms was estimated to be $^{57}Mn/Xe = 10^{-12}$. The counting rate of the PPAC was stable at 0.2 cps (count per second) throughout the measurements.

3 Results and discussion

The Mössbauer spectrum measured during implantation of ^{57}Mn into the Xe solid at 14 K is shown in Fig. 1. While Mössbauer spectra of ^{57}Mn in the Ar solid had only one peak of $^{57}Fe^+$ ($3d^7$) [9], the spectrum in this study had more than one peak. We fitted the spectrum assuming four singlet peaks; the Mössbauer parameters are summarized in Table 1. The most intense peak at $\delta = -1.89(5)$ mm/s was assigned to $^{57}Fe^+$ ($3d^7$). The second largest peak at $\delta = +0.82(6)$ mm/s was assigned to a ground state neutral Fe^0 ($3d^64s^2$) atom. Mössbauer parameters for $^{57}Fe^+$ ($3d^7$) and Fe^0 ($3d^64s^2$) were in good agreement with the values reported previously [8, 9]. The two other singlet peaks at $\delta = -0.04(7)$ mm/s and $\delta = -0.84(12)$ mm/s were not reported previously.

Emission Mössbauer spectra of ^{57}Co in a mixture Ar/Xe solid were reported by Van der Heyden, in which the doublet peak of the ground state $^{57}Fe^+$ ($3d^64s^1$; $\delta =$ 0.3 mm/s, $\Delta E_Q = 1.8$ mm/s) was observed [8]. The EC-decay of the ^{57}Co produced a defect in the fcc Xe lattice, and the non-cubic symmetry enhanced the transition from the excited $^{57}Fe^+$ ($3d^7$) states to the ground state $^{57}Fe^+$ ($3d^64s^1$). The $^{57}Fe^+$ ($3d^64s^1$) showed doublet peaks because of the asymmetry of the environment. On the other hand, the doublets corresponding to the $^{57}Fe^+$ ($3d^64s^1$) were not observed in our spectrum (Fig. 1). The β-decay of ^{57}Mn does not disturb the fcc lattice of the Xe solid, and ^{57}Fe stayed in cubic symmetry with the surrounding Xe atoms. The ground state $^{57}Fe^+$ ($3d^64s^1$) produced in cubic symmetry should show a singlet

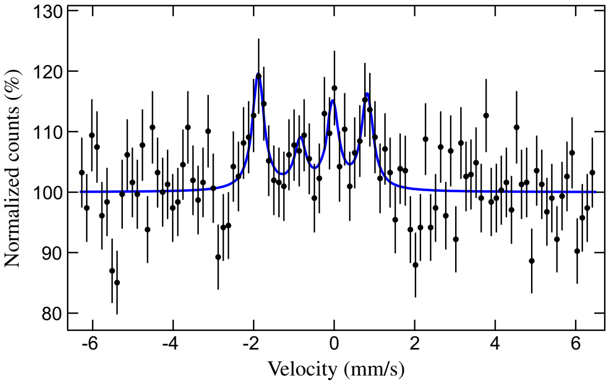

Fig. 1 In-beam Mössbauer spectrum of ^{57}Fe ($\leftarrow ^{57}Mn$) in a Xe matrix measured at 14 K

Table 1 Mössbauer parameters of ^{57}Fe ($\leftarrow ^{57}Mn$) in a Xe matrix at 14 K. Four singlet peaks were assumed to have the same linewidths

Species	δ mm/s	Γ mm/s	Area intensity
Fe^{+} $3d^7$	−1.89(5)	0.35(9)	34(8)%
Fe^{+} $3d^64s^1$	−0.04(7)		25(8)%
Fe^0 $3d^64s^2$	+0.82(6)		28(8)%
Fe^0 $3d^74s^1$	−0.84(12)		14(8)%

peak. Therefore, the peak at $\delta = -0.04(7)$ mm/s was assigned to ground state $^{57}Fe^{+}$ ($3d^64s^1$). The production mechanism will be discussed later.

Another singlet peak at $\delta = -0.84(12)$ mm/s corresponds to the species having an electron density between those of Fe^{+} ($3d^7$) and Fe^{+} ($3d^64s^1$), as the δ value is between the δ value of Fe^{+} ($3d^7$) and Fe^{+} ($3d^64s^1$). The isolated Fe atom that satisfies this condition is Fe^0 ($3d^74s^1$). The lowest excited state of a neutral free Fe^0 atom is Fe^0 ($3d^74s^1$), which is 0.86 eV above the ground state Fe^0 ($3d^64s^2$) [14].

The assignments of the four singlet peaks found in our experiment, $^{57}Fe^{+}$ ($3d^7$),$^{57}Fe^{+}$ ($3d^64s^1$), $^{57}Fe^0$ ($3d^64s^2$), and $^{57}Fe^0$ ($3d^74s^1$), were confirmed by comparing the observed δ values with calculated electron densities at the ^{57}Fe nucleus. Electron densities in iron nuclei $\rho(0)$ with various electronic configurations were calculated by J. P. Desclaux using Dirac-Folk calculations [15]. The observed δ values were plotted against the calculated $\rho(0)$ values (Fig. 2), and there was good correlation between the observed δ and the calculated $\rho(0)$.

In the case of ^{57}Mn in the Ar matrix, a charge transfer process between ^{57}Mn and surrounding Ar atoms was dominant to reduce Mn^{x+} ions, and thus $^{57}Mn^{2+}$ was trapped in the Ar solid for a duration comparable to its lifetime. The effects of free electrons in the Ar solid were negligible. The β-decay of $^{57}Mn^{2+}$ produced $^{57}Fe^{3+}$ ions followed by the charge transfer process with neighboring Ar resulting in the selective production of $^{57}Fe^{+}$ ($3d^7$) [9]. If we assume that charge transfer is the main process and the effects of free electrons are negligible in the Xe solid, $^{57}Fe^{+}$ ($3d^7$) should be produced selectively as follows. The first and second ionization potentials of Mn are $I^1_{Mn} = 7.44$ eV and $I^2_{Mn} = 15.65$ eV, whereas the first ionization potential of Xe is $I^1_{Xe} = 12.14$ eV; therefore, the implanted $^{57}Mn^{x+}$ ion should be stabilized as the $^{57}Mn^{+}$ ion. The β-decay of $^{57}Mn^{+}$ produces $^{57}Fe^{2+}$ followed by charge transfer with Xe atoms. The first and second ionization potential of Fe are $I^1_{Fe} = 7.91$ eV and $I^2_{Fe} = 16.20$ eV, and reduction by the charge transfer process produces an excited

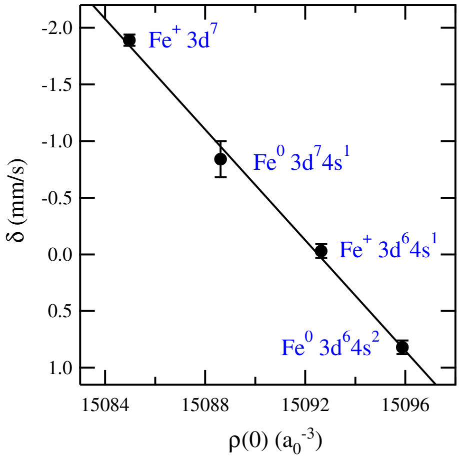

Fig. 2 Isomer shift δ obtained in the present work as a function of electron density at the nucleus $\rho(0)$ taken from Dirac-Fock calculations by J. P. Desclaux [15]

state $^{57}Fe^{+}$ ($3d^7$) as $I^2_{\mathrm{Fe}} - I^1_{\mathrm{Xe}} = 4.06$ eV. The β-decay of ^{57}Mn does not disturb the Xe lattice, and the transition from $^{57}Fe^{+}$ ($3d^7$) to $^{57}Fe^{+}$ ($3d^64s^1$) is forbidden in cubic symmetry. In practical terms, other species including $^{57}Fe^{+}$ ($3d^64s^1$), $^{57}Fe^{0}$ ($3d^64s^2$), and $^{57}Fe^{0}$ ($3d^74s^1$) were also observed in this study.

The effect of free electrons is not negligible in the Xe matrix [8] even though the electron mobility is very small [10]. The implanted $^{57}Mn^{x+}$ ion was stabilized as a neutral $^{57}Mn^{0}$ atom by the combination with free electrons supplied in the Xe matrix. The β-decay of $^{57}Mn^{0}$ produced excited $^{57}Fe^{+}$ without disturbing the fcc Xe lattice. The excited $^{57}Fe^{+}$ should have various electronic configurations other than $3d^7(^4F)$, for example $3d^64s^1$ (^4D). The charge transfer process with the surrounding Xe atoms could not reduce Fe^{+} ($I^1_{\mathrm{Fe}} < I^1_{\mathrm{Xe}}$), but combination with free electrons in the Xe solid occurred resulting in $^{57}Fe^{0}$ atoms. In this process, the ground state $^{57}Fe^{0}$ ($3d^64s^2$) was obtained. The reduction by free electrons also produced the excited $^{57}Fe^{0}$ ($3d^74s^1$) state. Thus, Fe atoms and ions with various electronic configurations were produced. In practical terms, the β-decay does not disturb the Xe lattice, and the transitions between the same parities were kept forbidden, resulting in the existence of the excited species, $^{57}Fe^{+}$ ($3d^7$) and $^{57}Fe^{0}$ ($3d^74s^1$).

4 Conclusion

The in-beam Mössbauer spectrum of ^{57}Mn implanted into a Xe solid at 14 K was measured. Four singlet peaks were observed, $^{57}Fe^{+}$ ($3d^7$), $^{57}Fe^{+}$ ($3d^64s^1$), $^{57}Fe^{0}$ ($3d^64s^2$), and $^{57}Fe^{0}$ ($3d^74s^1$). Combination with free electrons in the Xe solid stabilized the neutral $^{57}Mn^{0}$ atom, and β-decay of ^{57}Mn produced $^{57}Fe^{+}$ with various electronic states. The free electrons also reduced $^{57}Fe^{+}$ ions to produce $^{57}Fe^{0}$ atoms. The β-decay of ^{57}Mn does not disturb the surrounding cubic symmetry of the fcc Xe solid, and thus no doublet peaks were observed. The ion and atom with excited states, $^{57}Fe^{+}$ ($3d^7$) and $^{57}Fe^{0}$ ($3d^74s^1$), were observed because transitions to the ground states were forbidden in the surrounding Xe atoms with cubic symmetry.

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