



In-beam Mössbauer spectra for ^{57}Mn implanted sulfur hexafluoride

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Abstract

To investigate the interactions of ^{57}Fe atoms with sulfur hexafluoride SF_6 molecules, in-beam Mössbauer spectra were measured for ^{57}Mn implanted SF_6 at 9 K and 65 K. Isolated ^{57}Fe atoms or ions produced by β -decay were not trapped within the SF_6 matrix. At 9 K, monomeric FeF_2 and FeF_3 molecules were produced by reaction of ^{57}Fe with F atoms released by decomposition of the SF_6 molecules. When the temperature of the SF_6 solid was increased to 65 K, FeF_4 was formed in addition to FeF_2 and FeF_3 . Density functional calculations were performed to confirm the assignments of the candidate species identified in the Mössbauer spectra.

Keywords In-beam Mössbauer spectroscopy · Manganese-57 · Sulfur hexafluoride · Iron fluoride · Density functional calculations

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1 Introduction

In-beam Mössbauer spectroscopy using short-lived ^{57}Mn nuclei is a useful tool to study novel reactions in a solid material. When ^{57}Mn is implanted into hard solid materials such as ionic crystals, the ^{57}Fe atoms produced by β -decay of ^{57}Mn serve as a probe for lattice defects or local magnetic structural anomalies, which, in turn, reflect inter-actions with the surrounding host material [1]. However, when ^{57}Mn is implanted into low-temperature solids comprising reactive molecules, ^{57}Fe compounds may be trapped in the solid after reactions with the surrounding matrix. For instance, implantation of ^{57}Mn into ice resulted in the formation of $\text{Fe}(\text{H}_2\text{O})_4^{2+}$ and $\text{Fe}(\text{OH})(\text{H}_2\text{O})_3^+$, the new species being trapped in the ice lattice [2]. Also, when ^{57}Mn was implanted into low-temperature inert solids, single ^{57}Fe atoms or ions may be trapped in the matrix, and the chemical state of the ^{57}Fe atom after β -decay of ^{57}Mn in a solid Ar matrix was found to be Fe^+ with a $3d^7$ electronic configuration [3]. Sulfur hexafluoride (SF_6) is generally considered to be inert and stable, but the molecule releases F atoms as a result of reaction with highly energetic particles. Previously, we reported a study on matrix isolated iron fluorides produced by gas-phase reaction of laser-evaporated Fe atoms with SF_6 [4]. The products of the reaction were isolated in a low-temperature solid matrix and the Mössbauer spectra indicated that Fe_2F_6 molecules were produced in a pure SF_6 matrix, whereas FeF_3 and Fe_2F_4 were produced in a diluted SF_6/Ar matrix. Further, the dimeric species Fe_2F_6 and Fe_2F_4 were abundant and the monomeric FeF_3 species was a minor product of the gas-phase reactions.

In this study, the reactions induced by implantation of ^{57}Mn into solid SF_6 at low temperatures were investigated.

2 Experimental

The heavy iron synchrotron accelerator facility (HIMAC) at the National Institute of Radio logical Science (NIRS, Chiba, Japan) was used to perform the experiments. The ^{57}Mn nuclei were produced by a projectile fragmentation reaction of the primary beam of ^{58}Fe ions with a ^9Be target. A beam pulse of 1.2×10^6 particles was generated at 0.3 Hz and with a duration of 250 ms. The $^{57}\text{Mn}/\text{SF}_6$ mixture ratio was about 10^{-12} , so that all the ^{57}Mn atoms were isolated without any chance of dimer formation. A parallel-plate avalanche counter was employed as the detector, and noise was minimized by use of the β - γ anti-coincidence method [5]. A solid sample of SF_6 was prepared by introducing SF_6 gas via a flow controller onto a brass plate cooled to 9 K using a vibration-isolated pulse-tube He refrigerator. In-beam Mössbauer spectra for ^{57}Mn implanted into solid SF_6 were measured at 9 K and 65 K; the measurement times for the spectra were 18.5 and 22.8 h, respectively. The sign of the isomer shift δ values was the reverse of that normally obtained for conventional Mössbauer absorption spectra.

Density functional calculations were performed using the ORCA program [6, 7] to confirm the assignments of the species observed in the experiment. The hybrid functional Beck three parameter Lee-Yang-Parr (B3LYP) and the Ahlrichs triple-zeta valence basis sets with polarization functions (TZVP) and auxiliary basis (SARC/J) were employed for the calculation. To estimate the Mössbauer parameters, the core properties basis set CP(PPP) was employed for describing Fe atoms using calibration parameters reported elsewhere [8, 9].

3 Results and discussion

3.1 Mössbauer spectra

The in-beam Mössbauer spectrum for ^{57}Mn implanted into solid SF_6 at 9 K is shown in Fig. 1a. The spectrum was fitted by a combination of a singlet (A) and a doublet (B) (Table 1). When the ^{57}Mn was implanted into an inert noble-gas matrix (Ar [3] or Xe [10]), the ^{57}Fe atoms after β -decay of ^{57}Mn were stabilized as single Fe atoms ($3d^64s^2$) or Fe^+ cations ($3d^7$ or $3d^64s^1$). On the assumption that SF_6 is an inert matrix, the spectrum of the ^{57}Fe atom after β -decay of ^{57}Mn should be similar to the spectra observed in the case of inert noble gas matrices. However, the spectra for the species observed in the present experiment had very different Mössbauer parameters from those for Fe or Fe^+ . The isomer shift for species A ($\delta = -0.81(2)$ mm/s) was attributed to the high-spin divalent Fe^{2+} species. It is speculated that SF_6 was decomposed by reduction of the implanted $^{57}\text{Mn}^{n+}$ cations such that F atoms were released and reaction with Fe atoms produced FeF_2 . Species A was assigned as FeF_2 , despite the fact that Mössbauer experimental data for FeF_2 isolated in an inert matrix have not been reported. Another species B ($\delta = -0.56(3)$ mm/s; $\Delta E_q = 3.15(6)$ mm/s) was assigned as FeF_3 . The monomeric FeF_3 molecule has been reported [4] and the Mössbauer parameters obtained in this study were similar to the literature values. The aforementioned assignments were confirmed by density functional calculations as described later.

The Mössbauer spectrum was also measured at 65 K (Fig. 1b). The intensity of the peak decreased to 59% of that measured at 9 K due to the decrease of the recoil free fraction of soft

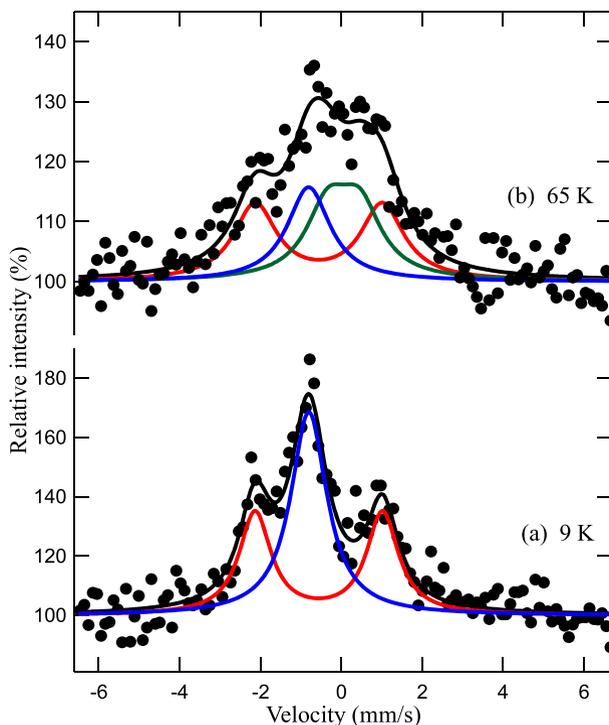


Fig. 1 In-beam Mössbauer spectra for ^{57}Mn implanted into solid SF_6 at (a) 9 K and (b) 65 K. The blue, red, and green lines denote singlet A, doublet B, and doublet C, respectively

Table 1 Mössbauer parameters for Fe implanted SF₆

Temp. (K)		δ (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	Area Int.
9	A	-0.81(2)	—	1.1(1)	66%
	B	-0.56(3)	3.15(6)	1.0(1)	34%
65	A	-0.81*	—	1.3(2) [†]	21%
	B	-0.56*	3.15*	1.3(2) [†]	39%
	C	0.1(2)	0.8(3)	1.3(2) [†]	40%

*The δ and ΔE_Q parameters were fixed at the value measured at 9 K

[†]The Γ values for A, B, and C were assumed to have the same value

SF₆ at the higher temperature. It was difficult to deconvolute the spectrum as it consisted of several components with broad peaks. Therefore, we fitted the spectrum by fixing the Mössbauer parameters for FeF₂ and FeF₃ (δ and ΔE_Q values measured at 9 K ignoring the second-order Doppler shifts) and assuming that the three components had the same peak widths Γ . As a result, a new doublet, species **C**, as well as FeF₂ and FeF₃ were found in the fitted spectrum (Table 1). The intensity of the FeF₃ peak was larger than that of the FeF₂ peak at 65 K, while the reverse was true at 9 K. Species **C** was found to be the major product (40%) at 65 K and production of this species may have been related to annealing effects whereby thermally stable species would be stabilized at the higher temperature. Also, the enhanced diffusion of F atoms in the SF₆ lattice at the higher temperature might have affected the formation and stability of species **C**. The isomer shift value for species **C** was in the same region as that for tetravalent Fe⁴⁺, so that species **C** was assigned as FeF₄.

3.2 Density functional calculations

Density functional calculations for candidate species observed in the Mössbauer spectra were performed. Calculations for the FeF_{*n*} (*n* = 1 to 6) species were carried out using B3LYP/TZVP and the results are listed in Table 2. The sign of the calculated isomer shift δ values is reversed compared to the values observed for conventional Mössbauer absorption spectra. The optimized structures for FeF₂, FeF₃ and FeF₄ are shown in Fig. 2. The geometries of the species were optimized and the stable structures were found to have high-spin states. The FeF₂ species had an *S* = 4/2 ground state with a linear structure (D_{∞h}), and state with a linear δ and ΔE_Q values were in good agreement with the experimental values. Though the Mössbauer spectra of monomeric FeCl₂ and FeBr₂ in low-temperature Ar matrices have been reported to possess small ΔE_Q values [11], the density functional calculations indicated that FeF₂ had a very small ΔE_Q value. To check the effects of the surrounding SF₆ lattice, the calculation for a FeF₂@(SF₆)₁₄ cluster (where FeF₂ is a substituent in the SF₆ lattice) was performed, the SF₆ lattice structure being taken from the solid structure reported [12] and where FeF₂ was a

Table 2 Calculated Mössbauer parameters using B3LYP/TZVP/CP(PPP)

Species		<i>S</i>	δ (mm/s)	ΔE_Q (mm/s)
FeF		5/2	-0.45	1.15
FeF ₂	A	4/2	-0.86	0.07
FeF ₃	B	5/2	-0.57	4.08
FeF ₄	C	4/2	-0.08	0.50
FeF ₅		3/2	+0.22	2.16
FeF ₆		2/2	+0.24	-1.36

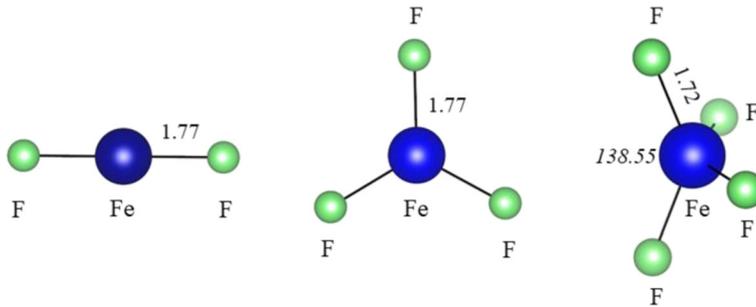


Fig. 2 Geometries of iron fluoride species (FeF_2 , FeF_3 and FeF_4) calculated by B3LYP/TZVP. Bond lengths are indicated in Angstroms and angles in degrees

substituent of SF_6 . The calculated Mössbauer parameters for the $\text{FeF}_2@(\text{SF}_6)_{14}$ cluster ($\delta = -0.86$ mm/s and $\Delta E_q = -0.03$) were almost identical to those for a single FeF_2 molecule, which indicates that the SF_6 lattice had very little effect on the environment of the Fe atom in FeF_2 . The optimized structure of FeF_3 had a plane triangular configuration (D_{3h}) with an $S = 5/2$ ground state. The calculated and observed δ values for FeF_3 were in quite good agreement with the calculated ΔE_q value, being slightly larger than the observed value.

The optimized structure of FeF_4 had D_{2d} symmetry with a $S = 4/2$ spin state, but the ΔE_q value was smaller than that observed in the spectrum, while the discrepancy of the ΔE_q values was smaller than the observed half-width Γ . The effects of the surrounding SF_6 lattice on FeF_3 and FeF_4 were also checked by calculating the Mössbauer parameters for $\text{FeF}_3@(\text{SF}_6)_{14}$ and $\text{FeF}_4@(\text{SF}_6)_{14}$ clusters, respectively. The calculated parameters for the clusters were identical with those for the isolated FeF_3 and FeF_4 molecules.

3.3 Formation reaction

In the experiment, highly charged $^{57}\text{Mn}^{n+}$ ions were implanted into the SF_6 solid. The $^{57}\text{Mn}^{n+}$ ions underwent reduction to stabilize the species via a charge transfer process between SF_6 and $^{57}\text{Mn}^{n+}$. The first ionization potential for SF_6 is $I^1\text{SF}_6 = 15.32$ eV. The first and second ionization potentials for Mn are $I^1_{\text{Mn}} = 7.44$ eV and $I^2_{\text{Mn}} = 15.65$ eV, respectively; therefore, $^{57}\text{Mn}^{n+}$ ions implanted into the SF_6 matrix underwent reduction, forming $^{57}\text{Mn}^+$ ions if charge transfer from SF_6 was the main process. Then, β -decay of $^{57}\text{Mn}^+$ ions produced $^{57}\text{Fe}^{2+}$ ions. Next, the $^{57}\text{Fe}^{2+}$ ions were reduced by charge transfer from the surrounding SF_6 , the first and second ionization potentials for Fe being $I^1_{\text{Fe}} = 7.91$ eV and $I^2_{\text{Fe}} = 16.20$ eV, respectively. The charge transfer process would have produced $^{57}\text{Fe}^+$ ions in the SF_6 matrix. Thus, the reduction processes for $^{57}\text{Mn}^{n+}$ and $^{57}\text{Fe}^{2+}$ cations would have produced SF_6^+ cations. Ionization of SF_6 molecules in the gas phase has been studied extensively [13], and it has been found that the production of SF_6^+ cations leads to numerous dissociative products [14]. Under the present experimental conditions, the ionized SF_6^+ cations would have readily undergone decomposition releasing F atoms, which in turn would have led to the production and trapping of FeF_2 and FeF_3 species in the SF_6 matrix.

Previous studies of laser-evaporated Fe atoms in an SF_6 atmosphere [4] did not result in the production of monomeric FeF_2 molecules; instead, the main products of the gas-phase reaction were dimeric Fe_2F_6 and Fe_2F_4 species. In the present study, however, the use of in-beam ^{57}Mn Mössbauer spectroscopy at 9 K provided very dilute conditions, such that monomeric FeF_2 and FeF_3 species were produced. When the temperature of SF_6 was increased to 65 K, the migration of F atoms within the SF_6 solid was enhanced, resulting in FeF_4 also being produced.

4 Conclusion

In-beam Mössbauer spectra for implantation of ^{57}Mn into solid SF_6 were measured at temperatures of 9 K and 65 K. A single ^{57}Fe atom or ion was not trapped in the SF_6 matrix despite the fact that SF_6 is generally considered to be an inert molecule. Monomeric iron fluoride molecules, FeF_2 and FeF_3 , were produced at 9 K by reaction of Fe with the F atoms released by the SF_6 molecules. When the temperature of SF_6 was increased to 65 K, new species assigned to FeF_4 were produced. Density functional calculations were performed to confirm the assignments, and the calculated Mössbauer parameters were in agreement with the experimental results. The calculations indicated that the FeF_2 , FeF_3 and FeF_4 species had linear ($D_{\infty h}$), triangular (D_{3h}) and tetrahedral (D_{2d}) structures, respectively.

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