Charged State of ^{57}Fe Atoms Following the Decay of ^{57}Co in Solid Xenon*

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Mössbauer studies with ^{57}Fe atoms following the decay of ^{57}Co in solid Xe find these atoms in two states: the stable Fe $3d^6 4s^2$ state and an unstable Fe$^+$ $3d^7$ state. The isomer-shift analysis yields $\Delta R/R = -(8.7 \pm 0.3) \times 10^{-4}$ for the 14.4-keV γ transition in ^{57}Fe. We obtain information about the charge-transfer mechanism and recombination time of Fe ions in solid xenon.

Mössbauer absorption experiments with rare-gas-matrix–isolated ^{57}Fe and ^{119}Sn atoms have been reported recently.[1-4] In these experiments the isolated atoms have been studied in the atomic configurations of the free atoms, e.g., ^{57}Fe in the $3d^6 4s^2$ atomic configuration.

It is well known that a nuclear electron-capture decay like that of ^{57}Co is followed by an Auger cascade which results in highly ionized atomic states of the daughter atom. Pollack[5] analyzed, for example, the Auger cascade in ^{57}Fe following the electron capture of ^{57}Co. This analysis shows that only 1% of the ^{57}Fe atoms will be found in the Fe state, 5% in the Fe$^+$ state, while the remaining 94% of the ^{57}Fe atoms will be in ionized states up to Fe^{6+}. The first observation of such Auger-produced charged states of ^{57}Fe was made in the decay of ^{57}Co in CoO.[6] Electron-capture aftereffects have also been found in several other ^{57}Co-doped Fe and Co compounds.[7]

Experiments with the β^- decay of ^{85}Kr in rare-gas matrices[8,9] have shown that the time for the recombination of the daughter ion ^{85}Rb$^+$ with a free electron in rare-gas matrices is much longer than 10^{-8} sec. This indicates that in the decay of ^{57}Co in rare-gas matrices, charged states of ^{57}Fe atoms should also be observed. The Mössbauer isomer shifts (IS) of such charged states of rare-gas-matrix–isolated ^{57}Fe atoms are new

calibration points in the plot of IS versus $\Psi^2(0)$ for ^{57}Fe [$\Psi^2(0)$ is the total relativistic electron density at the ^{57}Fe nucleus]. This offers the possibility of determining a reliable value for the relative change in the nuclear charge radius, $\Delta R/R$, for the 14.4-keV γ transition in ^{57}Fe.

The Mössbauer absorption spectra of rare-gas-matrix–isolated ^{57}Fe atoms have shown[2,3] that the Xe matrix has several advantages in comparison to the other rare-gas matrices. We decided, therefore, to isolate the ^{57}Co atoms in a Xe matrix. A detailed description of the apparatus and operating procedures for the rare-gas-matrix–isolation technique has been described elsewhere.[2]

The ^{57}Co in solid Xe source was obtained by evaporating a source consisting of 1.3 mCi ^{57}Co in Fe metal (4.4 mg iron, 90% enriched ^{57}Fe) out of an alumina crucible, mixing this ^{57}Fe/^{57}Co atomic beam with a stream of Xe gas, and condensing the mixed ^{57}Fe/^{57}Co-Xe beam on a liquid-helium–cooled Be disk. The deposition conditions produced, after 12 h, a ^{57}Fe/^{57}Co-doped Xe matrix with an iron atomic concentration φ ~ 1.1%, a total amount of ~ 60 μg/cm^2 iron (90% enriched ^{57}Fe), and ~ 10 μCi ^{57}Co in the Xe matrix. The counting rate for the 14.4-keV γ ray was 85 sec^{-1}.

The total effective absorber thickness of this absorber of ^{57}Fe in solid Xe is t ~ 0.6. Because

of this small t value, self-absorption and reso-
nant scattering within the ^{57}Co/^{57}Fe-doped Xe ma-
trix are negligible when the matrix is used as a
Mössbauer source.

There are two reasons why ^{57}Fe atoms were
added to the ^{57}Co atoms in the Xe matrix: (i) For
our matrix deposition condition the number of
^{57}Co atoms in the Xe matrix is much smaller than
the number of impurity species (N_2, O_2, etc.) in
the Xe matrix. These impurities result from the
finite residual-gas vapor pressure in the cryostat
($p \sim 10^{-7}$ Torr) during the matrix deposition.
Since N_2 and O_2 may have a high mobility in the
rare-gas matrices or on the rare-gas surface
during deposition, the ^{57}Fe atoms are added as a
"getter" to reduce the probability of a ^{57}Co-im-
purity interaction. (ii) The ^{57}Fe/^{57}Co-doped Xe
matrix can be used either as a ^{57}Co in solid Xe
source or as a ^{57}Fe in solid Xe absorber.

The experimental setups were the following:
fixed source (^{57}Fe/^{57}Co in Xe) and driven absorb-
er [K$_4$^{57}Fe(CN)$_6$·3H$_2$O, 0.25 mg/cm^2 ^{57}Fe] for the
source experiment; driven source (^{57}Co in Pd)
and fixed absorber (^{57}Fe/^{57}Co in Xe) for the ab-
sorption experiment.

The Mössbauer spectra obtained with the ^{57}Fe/
^{57}Co in solid Xe source are shown in Figs. 1(a)
and 1(b) for the two different matrix tempera-
tures 4.4 and 27 K. The time of measurement
for the 4.4-K spectrum was $\sim$250 h; for the 27-K
spectrum, $\sim$100 h. The spectra consist of two
resonances, one with an IS of $+0.76 \pm 0.02$ mm/
sec, the other with an IS of -1.77 ± 0.08 mm/sec.
(IS values are given relative to an iron metal ab-
sorber at 300 K.) Line positions are independent
of matrix temperature; however, linewidths
change with matrix temperature. Fig. 1(c) shows
the Mössbauer spectrum when ^{57}Fe/^{57}Co in solid
Xe is used as an absorber. This spectrum is
identical with the Mössbauer spectrum of ^{57}Fe
atoms in solid Xe as reported in earlier papers.[2,3]
The IS of the observed resonance is -0.76 ± 0.02
mm/sec relative to an iron metal absorber at
300 K. In order to make Figs. 1(a) and 1(b) and
Fig. 1(c) comparable, the Doppler velocity in
Fig. 1(c) is given relative to a K$_4$^{57}Fe(CN)$_6$·3H$_2$O
absorber at 300 K.

A comparison of Figs. 1(a) and 1(b) and Fig.
1(c) shows the following: (1) The stable iron
atoms [Fig. 1(c)] are only in one state. We as-
sume[2,3] that this is the neutral iron state Fe with
the atomic configuration $3d^6 4s^2$. (2) The atoms
produced by electron capture decay of ^{57}Co [Figs.
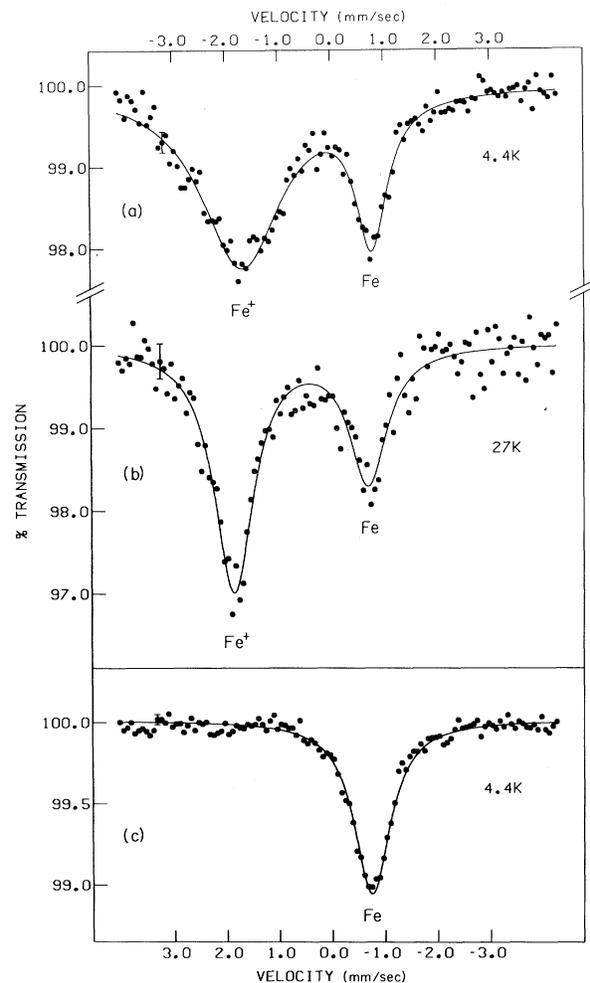1(a) and 1(b)] are in two different states. One of

FIG. 1. (a),(b) Mössbauer emission and (c) absorp-
tion spectra of a ^{57}Fe/^{57}Co-doped Xe matrix. Iron
atomic concentration $\sim$1.1%; 60-μg/cm^2 iron (90%-en-
riched ^{57}Fe); 10 μCi ^{57}Co. Matrix temperatures, 4.4
and 27 K. Doppler velocities relative to a K$_4$^{57}Fe(CN)$_6$
·3H$_2$O absorber.

these states has an IS which is, within the experi-
mental error, identical with the observed IS of
the stable ^{57}Fe atoms. Therefore, we assume
that this is the stable Fe state with the atomic
configuration $3d^6 4s^2$. The second state has a
more negative IS, i.e., a smaller electron densi-
ty at the iron nucleus than the neutral iron atom.
All reported ^{57}Fe IS lie between the two IS shown
in Figs. 1(a) and 1(b).

We interpret this second resonance as follows.
There are two possible recombination processes:
(I) Fe^{n+} + Xe $\rightarrow$ Fe$^{(n-1)+}$ + Xe$^+$, i.e., a charge-trans-
fer process; (II) Fe^{n+} + e^- $\rightarrow$ Fe$^{(n-1)+}$, i.e., the re-
combination with a free electron. Such a free
electron can either be a low-energy Auger elec-

tron or an electron produced by the ionization of the more energetic Auger electrons. The Xe^+ state (electron-hole state) resulting from the charge-transfer process will be quickly removed from the $Fe^{(n-1)+}$ ion by electron-hole diffusion. This means that after a time much shorter than τ_γ there will be no Xe^+-state atom as a nearest neighbor of $Fe^{(n-1)+}$. The charge-transfer process (I) will stop at the Fe^{2+} state since the recombination energy of Fe^{2+} is lower than the ionization energy of Xe. However, recombination with a free electron is possible up to the neutral state Fe. Since we see only one resonance, in addition to the Fe resonance, this must be an Fe^+ resonance. The lack of other resonances shows that the charge-transfer processes from Fe^{n+} to Fe^+ occur in times much shorter than the lifetime of the 14.4-keV nuclear excited state in ^{57}Fe ($\tau_\gamma \sim 10^{-7}$ sec).

There is in principle another possible mechanism for the production of neutral Fe: The Fe^+ state (electron-hole state) can resonate with a nearest-neighbor Fe state (for our Fe concentration $\sim 12\%$ of the ^{57}Co atoms have an Fe atom as a nearest neighbor). As a result of this resonance process the nuclear-excited ^{57}Fe atom can be in the neutral state during the γ emission. However, an Fe^+ as well as an Fe atom with an Fe nearest-neighbor atom will give Mössbauer resonances which do not coincide with the resonances of the isolated Fe^+ and Fe atoms (different IS, quadrupole splitting).[1-3] This process, therefore, will not affect the following discussion concerning the Fe^+/Fe line-intensity ratio.

The recombination time τ_R at matrix temperature T for the recombination of the Fe^+ state with a free electron to the Fe state is obtained from the intensity ratio of the Fe^+ resonance to the Fe resonance at temperature T, i.e.,

$$\frac{\tau_R(T)}{\tau_\gamma} = \left[\frac{(A\Gamma)_{Fe^+}}{(A\Gamma)_{Fe}}\right]_T \frac{f_{Fe}(T)}{f_{Fe^+}(T)},$$

where A is the amplitude, Γ the linewidth of the resonance, and f the nuclear recoilless fraction. The recoilless fraction $f_{Fe}(T)$ is known from the Mössbauer-absorption experiments with ^{57}Fe in solid Xe.[3] The effective Debye temperature (Mössbauer temperature) for the neutral Fe atom in solid Xe has been determined from these experiments to be $\Theta_M(Fe) = 59.2 \pm 4$ K.[3] We assume that the temperature dependence of the recoilless fraction $f_{Fe^+}(T)$ can be described by the Debye model with an effective Debye temperature

$\Theta_M(Fe^+)$. The analysis of the Fe and Fe^+ line intensities at the matrix temperatures 4.4 and 27 K [see Figs. 1(a) and 1(b)] yields $\tau_R(4.4\text{ K})/\tau_R(27\text{ K}) = 2.6 \pm 0.5$; $\tau_R(4.4\text{ K}) = (2.6 \pm 0.2) \times 10^{-7}$ sec; $\tau_R(27\text{ K}) = (1.0 \pm 0.2) \times 10^{-7}$ sec; $\Theta_M(Fe^+) = 90 \pm 20$ K.

The measured ratio $[\tau_R(4.4\text{ K})/\tau_R(27\text{ K})]_{meas} = 2.6 \pm 0.5$ is in good agreement with the theoretical value $[\tau_R(4.4\text{ K})/\tau_R(27\text{ K})]_{theor} = 2.5$ which one would expect if the recombination of Fe^+ to Fe takes place with thermal electrons. In that case $\tau_R(T) \sim \langle v(T)\rangle^{-1} \sim T^{-1/2}$, where $\langle v(T)\rangle$ is the mean thermal electron velocity at the matrix temperature T.

The effective Debye temperature $\Theta_M(Fe^+)$ is higher than the $\Theta_M(Fe)$ obtained from earlier measurements.[3] This can be explained in terms of a polarization of the Xe nearest-neighbor atoms of Fe^+, which results in a stronger coupling between the Fe^+ ion and the Xe atoms in comparison to the coupling between the Fe atom and the Xe atoms.

FeF_2 is the most ionic ferrous compound. Therefore, it is usually assumed[10,11] that the IS of FeF_2 is representative of the IS for the atomic configuration $3d^64s^0$. Since the IS differences are $\Delta\delta(Fe-Fe^+) = 2.53 \pm 0.08$ mm/sec and $\Delta\delta(Fe-FeF_2) = 2.32 \pm 0.02$ mm/sec,[12] we have to conclude that $\Psi^2(0)$ at the iron nucleus of the Fe^+ state in solid Xe is less than $\Psi^2(0)$ at the iron nucleus in FeF_2. That means either (A) the observed Fe^+ state in solid Xe is in the atomic configuration $3d^64s$ (the atomic ground-state configuration of the free Fe^+ ion)[13] but $\Psi^2(0)$ at the iron nucleus in FeF_2 is not at all representative of $\Psi^2(0)$ for the $3d^64s^0$ atomic configuration, or (B) $\Psi^2(0)$ at the iron nucleus in FeF_2 is a reasonable approximation of $\Psi^2(0)$ for the $3d^64s^0$ atomic configuration but the observed Fe^+ state in solid Xe is not in a $3d^64s$ but in a $3d^7$ atomic configuration. Since case (A) is very unlikely (the obtained $\Delta R/R$ value for the 14.4-keV γ transition would be unreasonably high), we assume case (B).

We cannot determine whether the observed Fe^+ state in solid Xe with the assumed atomic configuration $3d^7$ is the ground state of Fe^+ in the Xe matrix or an excited, metastable state of Fe^+ with an atomic lifetime much longer than the nuclear lifetime τ_γ. Since for the free Fe^+ ion the lowest excited $3d^7$ state is ~ 2000 cm^{-1} above the $3d^64s$ ground state[13] there has to be a substantial matrix perturbation to the Fe^+ states in order to make the $3d^7$ state the ground state of Fe^+ in the Xe matrix. The observed[14,15] small rare-gas–

matrix perturbation effects on the Fe atomic configurations $3d^6 4s^2$, $3d^6 4s 4p$, and $3d^7 4p$ make it more likely that the observed Fe^+ state is an excited, metastable state which is preferentially occupied by the charge-transfer process, i.e., $Fe^{2+} + Xe \rightarrow Fe^{+*}(3d^7) + Xe^+$. The difference in the recombination energy of Fe^{2+} (ionization energy of Fe^+) and the ionization energy of Xe^+ is $\Delta E_{ion} = E_{ion}(Fe^+) - E_{ion}(Xe) \sim 32\,000$ cm^{-1}.[13] The Fe^{+*}-$(3d^7 b^2 F_{7/2})$ state (using the notation of Ref. 13) is $E^* \sim 32\,000$ cm^{-1} above the $3d^6 4s$ ground state.[13] [The above given atomic level and ionization energies are free-atom (ion) values.] It is this $Fe^{+*}(3d^7 b^2 F_{7/2})$ state which will be preferentially occupied by the charge-transfer process (energy resonance, i.e., $\Delta E_{ion} \sim E^*$).

Nonrelativistic Hartree-Fock calculations[16] give for the difference in the nonrelativistic total electron density at the iron nucleus, $\psi^2(0)$, between the atomic configurations $Fe(3d^6 4s^2\ ^5D)$ and $Fe^+(3d^7)$, the value $\Delta\psi^2(0) = 8.0$ a.u. Correcting $\psi^2(0)$ with the relativity factor $S(Z) = \Psi^2(0)/\psi^2(0)$ as given by Shirley[17] ($S = 1.29$ for iron) we get $\Delta R/R = -(8.7 \pm 0.3) \times 10^{-4}$ for the 14.4-keV γ transition in ^{57}Fe. The error includes only the experimental error; uncertainties in the calculation of $\psi^2(0)$ were not taken into account.

The IS difference between the rare-gas-matrix-isolated Fe and FeF$_2$, together with this new $\Delta R/R$ value, gives for the difference in $\psi^2(0)$ between Fe and FeF$_2$ the value 7.35 ± 0.25 a.u. The difference in $\psi^2(0)$ between $Fe(3d^6 4s^2\ ^5D)$ and $Fe^{2+}(3d^6$ $^5D)$ as obtained in Ref. 16 is 7.0 a.u., i.e., $\psi^2(0)$ at the iron nucleus in FeF$_2$ is 0.35 ± 0.25 a.u. less than $\psi^2(0)$ in the free $Fe^{2+}(3d^6\ ^5D)$. This can be explained by a small increase of the $3d$-shielding effect for Fe^{2+} in FeF$_2$ in comparison to the free Fe^{2+}.

This first report of a Mössbauer experiment with ^{57}Co atoms in solid Xe shows the possibilities of such a type of experiment. Not only are reliable $\Delta R/R$ values for Mössbauer γ transitions obtained but also such solid-state effects as charge transfer and recombination of impurity ions with free electrons can be studied.

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