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by J. Fenger

December 1971

A Mössbauer-Beam Experiment and its Possible Applications in the Study of Chemical Effects of the ^{56}Fe(n, γ)^{57}Fe Reaction

by

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Abstract

The ^{56}Fe(n, γ)^{57}Fe reaction can be used to populate the 14 keV Mössbauer level in ^{57}Fe. This offers in principle a possibility of non-destructive investigation of the chemical effects of neutron capture-γ recoil in iron compounds. Targets of $K_4Fe(CN)_6 \cdot 3H_2O$ and $Fe(COO)_2 \cdot 2H_2O$ were irradiated in a neutron beam and simultaneously used as sources in a Mössbauer experiment. No resonances were detected with $K_4Fe(CN)_6 \cdot 3H_2O$, but weak resonances from $Fe(COO)_2 \cdot 2H_2O$ suggest that in this compound some recoil-^{57}Fe is stabilized as divalent iron. Various improvements of the experimental set-up are considered; however, it appears that such experiments are not very promising from a "hot-atom chemistry" point of view.

CONTENTS

1. INTRODUCTION

When an atomic nucleus absorbs a neutron, the binding energy is emitted in the form of one or a few capture-Y-quanta. Hereby the daughter nucleus suffers a recoil, which may typically correspond to a kinetic energy of a few hundred electron volts. In a solid, the nucleus recoils out of its lattice position, carrying with it most of its electrons. The initial velocity of such a recoil atom is of the order of 10^{14} A/s, its range is of the order of 10 A, and consequently it comes to rest within about 10^{-12} s.

The study of the chemical fate of recoil atoms in solids poses various problems. Normally the samples are irradiated in nuclear reactors, which give not only thermal-neutron but also Y-irradiation. Radiolytic effects, which may mask the effects of nuclear recoil, make short irradiation times and consequently low neutron doses necessary. The molar concentrations of recoil atoms which can thus be obtained is extremely low - typically 10^{-10}. Fortunately the nuclei formed by neutron capture are often radioactive. If the irradiated samples are dissolved, it is therefore possible by radio-chemical methods to investigate some chemical effects in the solid. Obviously such analyses must take place some considerable time after the nuclear event, and further they can only detect species which are stable in the solvent.

In recent years various attempts have been made to apply non-destructive physical methods in studies of chemical effects of nuclear reactions. For (n, Y) reactions the use of a Mössbauer spectrometer on line with a reactor is a tempting possibility, since not only non-destructive, but also immediate analyses are - at least in principle - possible.

Mössbauer experiments are normally based on radioactive sources, but it is also possible to populate Mössbauer levels by inducing nuclear reactions - e. g. (d, p)-reactions, Coulomb excitations, and also neutron capture. The principle in most of such experiments is the same and appears from fig. 1.

A beam of particles (here thermal neutrons) hits a titled target and induces the nuclear reactions. The target serves as a source in a Mössbauer experiment which - in order to reduce the background - is performed with the axis forming a right angle with the beam. In experiments based on (n, Y)-reactions the sequence of events is the following: A neutron is absorbed in a nucleus, and capture-Y-quanta are emitted in a cascade which with a certain probability passes the Mössbauer level. Since the stopping time of recoil atoms is much shorter than the lifetime of Mössbauer levels,
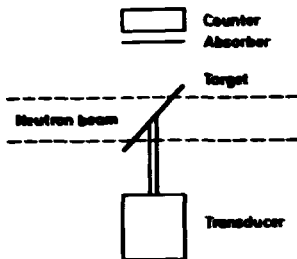
Fig. 1. The principle in a "Mössbauer-beam" experiment.

the atom will recoil out of its lattice site and again come to rest before the
Mössbauer quantum is emitted. A measurement of "Mössbauer parameters"
(isomer shift etc.) might therefore yield information on the chemical form
and (or) the surroundings in which the recoil atom is stopped.

In our experiments iron was chosen as a convenient Mössbauer nucleus,
which can be formed by the $^{56}Fe(n, \gamma)^{57}Fe$ reaction. Berger has previously
shown that beam experiments are possible with iron alloys [1], and he has
also in a single case used a target of $FeSO_4 \cdot 7H_2O$ [2]. Such compounds,
however, are too simple from the point of view of "hot-atom chemistry"; it
was therefore decided to perform experiments with targets of materials in
which some chemical reactions could be expected. $K_4Fe(CN)_6 \cdot 3H_2O$ and
$Fe(COO)_2 \cdot 2H_2O$ were chosen, since we had previously investigated the
chemical effects of the $^{58}Fe(n, \gamma)^{59}Fe$ reaction in these compounds by con-
ventional radiochemical methods [3,4]. Therefore it might be possible to
compare results obtained by different experimental techniques on similar
nuclear reactions. We have further studied the chemical effects of
$^{57}Co(EC)^{57}Fe$ reactions by Mössbauer spectroscopy [3,4,5] and might
thus have the possibility of comparing the effects of different nuclear reac-
tions.

The present report mainly deals with the technical aspects of the beam
experiment, but it will appear that the expectations expressed above have
so far only been fulfilled to a very modest extent.

2. EXPERIMENTAL TECHNIQUES AND PROCEDURES

Various preliminary experiments were performed in the DR 2 reactor, but the measurements reported here were made in the DR 3. Most of the parts of the experimental set-up had been designed for - and used in - previous experiments; technical details can therefore be found in the references.

2.1. Neutron Beam Facility

The beam facility, comprising collimators, bismuth filter, evacuated flight tube, etc. was essentially the same as constructed by C. J. Christensen et al. [6] for use in the measurement of the neutron half-life. In order to facilitate the operation the bismuth filter [7] was used without cooling; the reduction in neutron flux was compensated for by using a thicker water scatterer and a modified collimator. The neutron flux at the position of the target is constant over a diameter of 4 mm and then falls linearly with the distance from the centre. The total diameter of the beam is 38 mm.

The neutron flux was measured in the beam centre with a circular, 1 cm^2 gold foil; then the total beam strength was calculated by integrations of the beam profile over the gold foil area and over the total beam cross section respectively. The result, $1.8 \cdot 10^8$ n/s, permits a calculation of the number of neutron absorptions in target nuclei from tabulated values for thermal neutron cross sections. It is, however, only a formal quantity, since - owing to the bismuth filter - the velocity of the neutrons in the beam does not follow a Maxwell distribution. An estimate [8] of the beam strength based on previous measurement and corrections for the effects of the modifications in the facility yields a value of $6.5 \cdot 10^7$ n/s. With an assumed mean neutron velocity of 1000 m/s [6] this corresponds to a formal beam strength of $1.4 \cdot 10^8$ n/s.

2.2. Targets and Target Chamber

Targets were prepared from analytical grade $K_4Fe(CN)_6 \cdot 3H_2O$ and $FeC_2O_4 \cdot 2H_2O$ which were finely powdered and cast in a minimum of polyester-styrene to make 4 by 6 cm plates containing about 100 mg/cm^2 of the compounds. Mössbauer measurements with the target plates as absorbers ensured that no chemical changes were induced by the casting (section 3.1). It was also attempted to make an absorber of $FeSO_4 \cdot 7H_2O$ by this method, but the iron was oxidized.

The target plates were suspended in a light aluminium holder (fig. 2) which was moved by a transducer (section 2.3). The beam is essentially
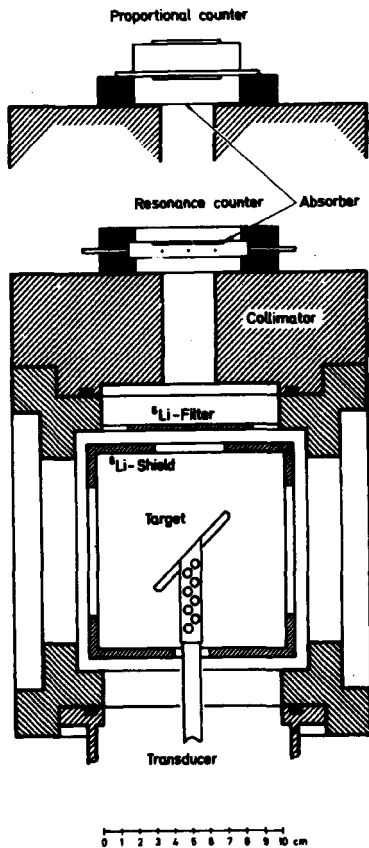
Fig. 2. A cut through the Mössbauer part of the beam experiment (slightly simplified). The neutron beam comes from a collimator attached to the left flange and leaves the target chamber through a tube attached to the right flange. Two alternative counters are shown.

free of γ's and fast neutrons, but neutrons scattered in the target material and subsequently absorbed in the surroundings caused a serious increase in the γ-background. In order to suppress this effect, the target was placed in a chamber covered on the inside with ^{6}LiF and directly connected with the evacuated collimator. An exit window facing the counter was covered with a neutron filter containing 200 mg ^{6}LiF/cm^2. This stopped most scattered neutrons and reduced the 14 keV radiation by only 15-20%.

2.3. Mössbauer Spectrometer

The "Mössbauer part" of the experimental set-up was with some modifications conventional. The resonances were expected to be weak and broad, and long counting times were anticipated; therefore it was obvious to use a constant acceleration system operating in a multiscaler mode.

The transducer (constructed by J. Olsen and K. C. Nyvang Nielsen) was of the "Kankeleit type" [9] and based on a pair of Philips "Ticonal" loud-speaker magnets. Only it was found that bronze springs, normally used for suspending the moving parts, had disturbing acoustic resonances; they were therefore replaced by suspensions for loudspeaker cones.

The velocity drive (constructed by O. Frost Hansen) was based on a modified Nuclear Data 130A, 512 channel analyser. The read-out oscillator counts the channel scaler forth and back between channels 0 and 255; the channel number is fed through the "Horizontal deflection" digital to analogue converter, and the resulting triangular voltage is used as a reference for the transducer movement. A pulse from the counting system is stored in the channel indicated by the channel scaler; its number is proportional to the transducer velocity. If desired, the counts registered during the positive and negative accelerations can be stored separately in channels 0-255 and 256-511 respectively. A sequential circuit prevents changing of channel during registration of a counting pulse. The relative differential linearity, defined as variation in channel width in units of time, is below ± 0.5 o/oo.

2.4. Counters

Various counters were considered. First a special proportional counter constructed by Kroy and Egidy [10] and also used by Berger [1] was tried. It consists of a central "signal" counter surrounded, in the same container, by a ring of small "shield" counters. By registering only anticoincidences between the "signal" and the "shield" counters, it is possible to reduce the wall effects appreciably. However, the anticoincidence rate was found to be

very low; further it was - with the electronics available - not possible to keep the counter stable over the long counting periods necessary (2-3 weeks).

Solid-state detectors have a high resolution, and therefore a low background in a counting channel can be obtained. But they need a cooling device, and it was assumed that this could give rise to increase in the background due to capture-γ-quanta.

Two counters were actually used for recording spectra (fig. 2): a commercial xenon-filled proportional counter, only 12 mm thick and furnished with an exit window (20th Century Electronics type PX 130 JJ), and a resonance counter, specially developed for use in source experiments [11] . Since a resonance counter registers a resonant absorption via the de-exitation of the 14 keV level in the absorber, it shows peaks at resonance and not dips.

2.5. Data Treatment

All the Mössbauer spectra were recorded in the "unfolded" multiscaler mode and resolved with a "least-squares" fitting programme [12] originally developed by A.J. Stone for the "Titan" computer in Cambridge, England. The programme assumes Lorentian line shapes and a base line modified by a linear drift and a sine wave. Some or all parameters can be fitted, constrained to fixed values, or constrained to be equal.

The well-known [e.g. 13] absorber spectrum of $Fe(COO)_2 \cdot 2H_2O$ versus a $Pd(^{57}Co)$ source and source spectrum of $Fe(^{57}Co)(COO)_2 \cdot 2H_2O$ versus a stainless-steel absorber were used for calibration as previously [5] described.

Visual inspection of the spectra recorded with the neutron beam on the targets did not reveal any resonances. It was then attempted to add the contents of the channels in sets of four (a small computer programme with display was made by C. Suusgaard); for the $Fe(COO)_2 \cdot 2H_2O$ target barely visible signals appeared, but they were not sufficiently accurately determined to serve as estimates for the computer fit. The fitting procedures were therefore started with estimates based on normal source and absorber spectra.

3. RESULTS

Before and in between the beam experiments proper, various control experiments were performed. It soon became evident that no resonances

could be observed with $K_4Fe(CN)_6 \cdot 3H_2O$; the efforts were therefore con-
centrated on the $Fe(COO)_2 \cdot 2H_2O$ target. All the control experiments
described below refer to this compound. The calculations of the assumed
signal to background ratio for the $K_4Fe(CN)_6 \cdot 3H_2O$ was performed on the
basis of older measurements [3] and the values obtained for $Fe(COO)_2 \cdot 2H_2O$.

3.1. Control Experiments

A series of trivial checks on the stability of the electronics, the align-
ment of the beam, etc. will not be described. Only two checks on the target
are special for this experiment.

Fig. 3A is an absorber spectrum of the target plate; it is fitted with a
quadrupole doublet of two Lorentzian lines constrained to have equal intensi-
ty and width. The fit is not quite satisfactory, as one of the lines is actually
slightly stronger than the other; this is in agreement with the previous ob-
servation [14] that the ferrous oxalate prepared by us contains of the order
of 1% ferric iron. Attempts to fit the spectrum with more than two lines
failed. We therefore conclude that - within the accuracy of the measure-
ments - the $Fe(COO)_2 \cdot 2H_2O$ is unaffected by the casting (section 2.2).

Fig. 3B is a spectrum of a $Pd(^{57}Co)$ source glued to the target plate
and recorded with the resonance counter. The peak to base line ratio is
about 600%; this figure was not exceeded in normal laboratory experiments
with the resonance counter, and we therefore conclude that the large target
plate and its support do not have disturbing oscillations. On the other hand,
it is noted that the experimental points correspond to a curve which is
slightly broader than the fitted Lorentzian curve; actually the resonance
can be fitted better with a narrow doublet. The self-absorption in the ab-
sorber is probably negligible since the effective thickness is only about 0.1
mg/cm^2 [11]. We therefore assume that the line broadening is caused by
a diminished acceleration around zero velocity due to the heavy load of the
transducer; this error has no significance in the measurement of the (pre-
sumably) broad lines in the beam experiment.

3.2. Estimate of the Expected Signal to Background Ratio

Since - in nature of things - we do not know the number of the reson-
ances, their width, etc. for a given compound, it is not possible to predict
unambiguously the signal to background ratio. The following estimates for
the $Fe(COO)_2 \cdot 2H_2O$ target are therefore based on the assumption that the
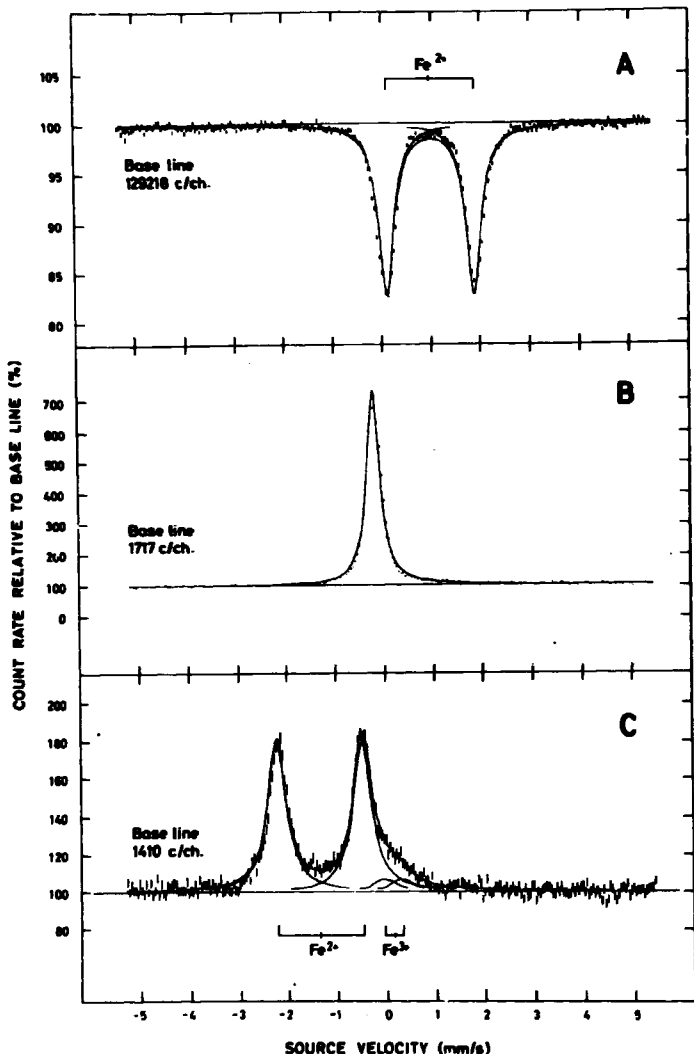Mössbauer spectrum of the target in the beam experiment is similar to the

Fig. 3. Control and calibration spectra recorded with the spectrometer in the beam experiment; only one of the two parts of the "unfolded" spectra is presented. _A_. The $Fe(COO)_2 \cdot 2H_2O$ target measured as absorber versus a $Pd(^{57}Co)$-source with the proportional counter. The spectrum is fitted with a single $^{57}Fe^{2+}$-doublet. _B_. A $Pd(^{57}Co)$-source glued to the $Fe(COO)_2 \cdot 2H_2O$ target and measured versus the stainless-steel absorber in the resonance counter. _C_. A $Fe(^{57}Co)(COO)_2 \cdot 2H_2O$ source measured versus the stainless-steel absorber in the resonance counter. A $^{57}Fe^{2+}$ doublet with a splitting of 1.74 mm/s accounts for 90% of the ^{57}Fe; a narrow doublet with a splitting of 0.35 mm/s and a relative intensity of 10% is ascribed to $^{57}Fe^{3+}$ [4].

one recorded with a ^{57}Co-doped source. This assumption is to some extent justified by the observation [4] that after both ^{58}Fe(n, γ)^{59}Fe and ^{57}Co(EC)^{57}Fe the iron is found largely as Fe^{II}.

For the conventional proportional counter the estimation is straight-forward. Fig. 4 shows part of the capture-γ-spectrum recorded with the complete experimental set-up, only the absorber has been removed. For comparison is also shown the 14 keV γ-line recorded with a ^{57}Co source glued to the target.

It appears that 14 keV capture-γ-quanta will account for only about 10% of the counts registered in a reasonably narrow channel around 14 keV. Since oxalate sources normally have resonance dips of about 8% [11], the resonances in the beam experiment may be 1/2-1%, for a line width of about 0.8 mm/s.

For the resonance counter the procedure is more complicated since we do not know the efficiencies of registration of Mössbauer-γ-quanta and other γ-quanta respectively. First an oxalate source (prepared by K. E. Siekier-ska) was absolute calibrated (by J. Olsen), and the spectrum was recorded
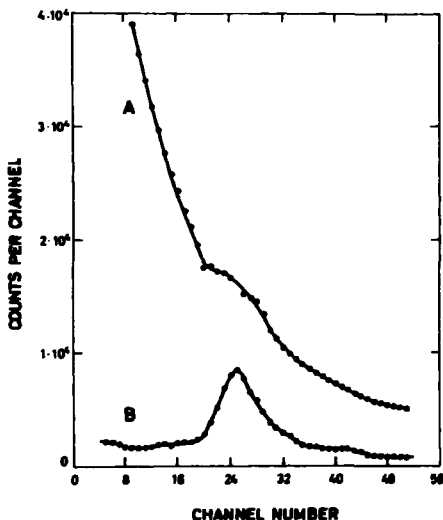

Fig. 4. Part of the γ-spectrum showing the 14 keV line recorded with a PX 130 JJ detector in the beam experiment. A: capture-γ from a Fe(COO)$_2$ · 2H$_2$O-target. B: the target replaced by Fe(COO)$_2$ · 2H$_2$O doped with ^{57}Co.

in the complete Mössbauer spectrometer - only with the source substituted for the neutron-irradiated target. An example of such a spectrum is shown in fig. 3C. From this it is calculated that for the specific velocity scan, geometry, etc. the probability that a decay from the 14 keV level will be registered is $3.3 \cdot 10^{-8}$.

From the formal beam strength (section 2.1), the content of ^{56}Fe in the target, and the tabulated neutron capture cross section for ^{56}Fe (2.75b [15]) it is calculated that $2.1 \cdot 10^5$ neutrons are captured per second. Only about 50% of the γ-cascades pass the 14 keV level [15], thus the number of 14 keV decays in the target per second is $1.1 \cdot 10^5$ (disint. s^{-1}). The number of decays registered per second is therefore - still assuming the same behaviour of the source and the target - $3.6 \cdot 10^{-3}$ (counts/s). Multiplication of this figure by the counting time gives an estimate of the resonance peak areas which is independent of the background count rate. With the actual background and with the same line width as in fig. 3C the peak to background ratio should be 0.9%, i.e. slightly better than with the proportional counter.

For the $K_4Fe(CN)_6 \cdot 3H_2O$ target the values should be about half that of the oxalate target.

3.3. Mössbauer Beam Spectra

A single experiment was made with the $K_4Fe(CN)_6 \cdot 3H_2O$ target and the resonance detector, but the subsequent computer fit showed that the base line did not differ significantly from a straight line. It is estimated that any resonance must have a peak value lower than about 25% of the calculated value.

For the $Fe(COO)_2 \cdot 2H_2O$ target spectra were recorded both with the proportional and the resonance counter; the results of two runs are shown in fig. 5. The recording of the spectra was interrupted by checks, i.a. of the electronics; the effective counting times are indicated in the figure caption.

The fitted parameters are shown in the figure. In both cases a doublet has been assumed with initial line positions equal to the ones observed with doped sources (fig. 3C); Only for the spectrum recorded with the proportional counter was it possible to let the line positions free without causing the fitting process to diverge. It is noteworthy that the fitted resonances have the right - and different - signs; this indicates that the very weak and broad lines do actually represent a Mössbauer effect and not a periodic
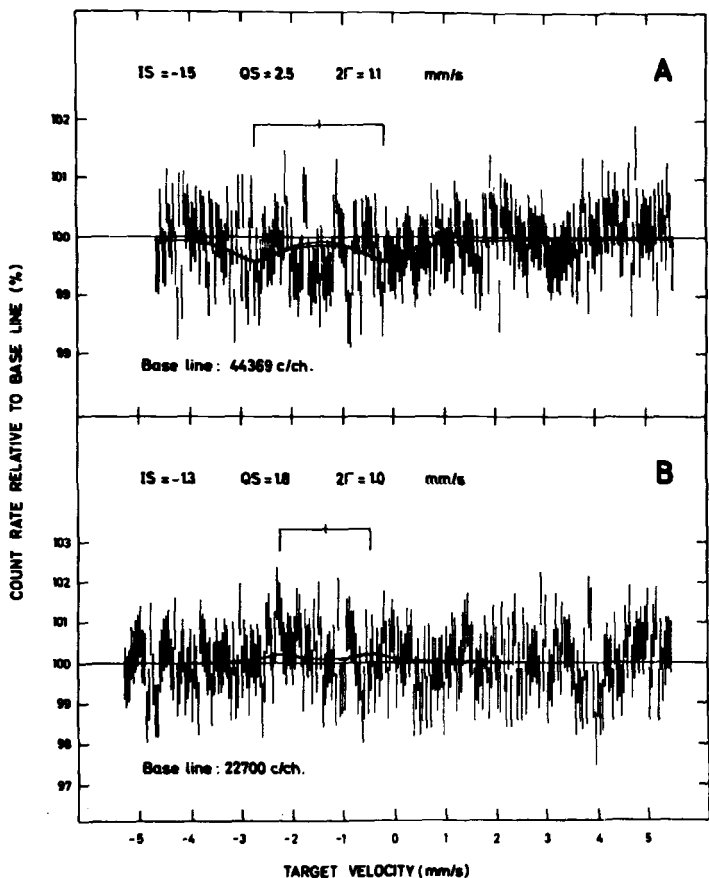
Fig. 5. Mössbauer-beam spectra of $Fe(COO)_2 \cdot 2H_2O$; only one part of the spectra is shown. A. Recorded with the proportional counter; total counting time: 346 h. B. Recorded with the resonance counter; total counting time: 533 h.

variation in the base line. The resulting parameters only allow the qualitative conclusion that some of the detected ^{57}Fe must be in the form of Fe^{2+}. The dips and peaks are significantly lower than estimated in section 3.2, and although the lines are broader, it appears that the intensities are smaller. For the resonance counter the estimated total intensity is 6900 counts, but the fitted peaks only represent about 3600.

4. DISCUSSION

The results presented in section 3.3 are consistent with our previous radiochemical investigations of the chemical effects of the $^{58}Fe(n, \gamma)^{59}Fe$ reaction. With $Fe(COO)_2 \cdot 2H_2O$ about 90% of the recoil-^{59}Fe was found as ferrous ions or weak ferrous-oxalato complexes [4]. With $K_4Fe(CN)_6 \cdot 3H_2O$, on the other hand, only 20-25% of the recoil-^{59}Fe was found as cyano complexes; we further had evidence that a substantial fraction of the cyanide complexes was formed by a recombination reaction, the time constant of which is not known [3]. Therefore only a small fraction of the recoil-^{57}Fe in the $K_4Fe(CN)_6 \cdot 3H_2O$ target may be in regular lattice positions when the 14 keV-quantum is emitted.

Similar observations have been made in other beam experiments where the Mössbauer effect seems to decrease with the complexity of the target material. Thus e.g. Coulomb excitation with α-particles yields a "full" Mössbauer effect in targets of α-iron, but only half the expected value in Fe_2O_3 [16]. It is therefore concluded that (op. cit.) "in an open lattice containing a mixture of atoms of differing masses the probability of a replacement collision would be expected to be reduced by the very nature of the lattice geometry".

The risk of "losing" some recoil atoms is a serious drawback if this type of experiment is to be applied in the study of chemical effects of neutron capture recoil. It will not only result in low signals, but also make a direct comparison with radiochemical analysis impossible.

Another point is that with the available techniques the accuracy of the measurements is insufficient for analysis of more complex systems. We considered a complete redesign of the experimental set-up including cooling of the bismuth filter, different collimators, and a better counter - e.g. of the type used by Berger [1, 10]. This could probably improve the resonance to base line ratio by a factor of 3-5 without reducing the overall counting rate seriously. Nevertheless, this would still be insufficient for studies of systems like the iron-hexacyanides where the spectra are difficult to

resolve unambigously even in experiments with relatively strong sources [e. g. 3]. Therefore a more sophisticated approach is necessary; one possibility is to have a neutron beam so intense that it is possible to register 14 keV Mössbauer quanta in coincidence with one of the prior capture-γ's in the decay of recoil-^{57}Fe [17]. But it is questionable whether such experiments may be justified from a hot-atom chemistry point of view, and whether the possible result can be correlated with results from other experiments.

ACKNOWLEDGEMENTS

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