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The Mössbauer Effect and the Study of the Chemical Consequences of Nuclear Transformations

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The present review deals with one of the most important branches of radiochemistry, of considerable practical and applied importance (the preparation of "labelled" compounds, the enrichment of radioactive isotopes) and scientific and theoretical interest. An understanding of processes involving atoms which have undergone a nuclear transformation in the solid phase will make it possible to solve many problems of the physics and chemistry of the solid state. The bibliography contains 151 references.

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I. INTRODUCTION

The history of the study of so-called "hot" atoms, or "recoil atoms" dates from the discovery of Szilard and Chalmers[1]. The extensive practical development of reactor and cyclotron irradiation made the preparation of the radioactive isotopes of many elements and the study of the chemical effects accompanying radioactive decay or the course of a nuclear reaction readily attainable. The forms in which the recoil atoms are stabilised are determined by dissolving the irradiated or labelled solid specimen, followed by radiochemical analysis of the solution containing the radioisotope formed. This method of study is general in character and is obligatory; the concentrations of recoil atoms are so small that the observation of their chemical behaviour is possible in principle only if use is made of their radioactivity. So long as we are interested in practical problems (for example the enrichment of isotopes) no particular objections can be made to the use of an appropriate solvent and carriers. This method, however, acts as a brake on the development of theories of the mechanism and the forms in which recoil atoms are stabilised in the solids themselves. In fact, in general it is impossible, having detected particular chemical forms of the element being studied in solution, to reach the unambiguous conclusion that their behaviour in solution is a consequence of only the radioactive decay or a nuclear reaction in the solid phase. They may obviously also be a consequence of the reaction of the primary decay fragments with the solvent or with one another. The introduction of additional methods of investigation (the study of thermal annealing, the influence of the conditions of dissolution, etc.) can also give complete information on the true state of recoil atoms in a crystal lattice. It is obvious only that the interpretation of results from the chemical effects of nuclear transformations, obtained by these methods, requires an exceptionally careful attitude towards the dissolution procedure. There arises the complex problem of the correspondence between the forms of stabilisation in the solid and in the solution. Unfortunately, most radiochemical studies are carried out without even an attempt to take account of, or even to assume, the possible consequences of dissolution.

It is clear that the introduction of any experimental method which does not require the dissolution of a substance and which gives information on the behaviour of recoil atoms directly in the solid phase is extremely desirable. This additional possibility was provided for radiochemistry by Mössbauer's discovery of the phenomenon of nuclear gamma-resonance (NGR). Since the production of "Mössbauer" levels is always a consequence of some preceding radioactive decay (β-decay, α-decay, K-capture, isomeric transition) or nuclear reaction [(n,γ), (a,p), Coulombic excitation], it may be concluded that emission Mössbauer spectroscopy can be used successfully to study the chemical consequences of nuclear transformations in solids.

Several advantages of the NGR method for the solution of chemical problems can be listed.

1. The forms in which the recoil atoms are stabilised are studied directly in the solid phase.
2. The conditions of Mössbauer experiments are standardised and reproducible (unlike radiochemical techniques, with countless variations in the conditions of irradiation, dissolution, etc.).
3. The observations are made in a range of temperatures (from helium temperatures to $\sim 1000^\circ$K) which is difficult to attain in the irradiation of substances for radiochemical purposes in the usual form, particularly with subsequent chemical treatment of the target.
4. The consequences of a nuclear transformation are studied in a time interval of 10^{-7}–10^{-9} s. These intervals are fairly long compared with the duration of the electronic and relaxation processes accompanying the nuclear transformation, but they are still shorter by many orders of magnitude than the time intervals attainable in radiochemistry. Thus the systems studied are "protected" from the annealing phenomena which take place intensively in many instances at the ordinary temperatures and duration of treatment of the targets.

Although almost all information on the NGR method has been obtained by specialist physicists and has not dealt explicitly with radiochemical problems, it is possible to summarise the results obtained and to analyse them from the viewpoint of radiochemistry. Our aim is to discuss the possibilities provided by the use of the Mössbauer effect in the solution of radiochemical problems.

The present review consists of two sections, one of which is devoted to an NGR study of the relaxation times and forms of stabilisation of Mössbauer atoms produced by nuclear transformations characterised by low values of the recoil energy (K-capture, isomeric transitions, and β-decay). The other section is devoted to an examination of the processes of energy loss by recoil atoms during nuclear reactions [(n,γ), (d,p), Coulombic excitation] involving the formation of atoms with high energy. A separate paragraph gives some information on the parameters of NGR spectra required for the subsequent discussion (a more detailed examination of the problems of NGR theory can be found in a number of monographs[2-4]).

II. MÖSSBAUER EFFECT

Let us consider the emission of a gamma-quantum by a nucleus which is in an excited state and is rigidly fixed in a crystal. In this instance the recoil momentum is absorbed not by an individual nucleus, but by the whole crystal, so that the expression for the recoil energy E_R is written in the form

$$E_R = \frac{E_0^2}{2Mc^2},$$

where E_0 is the energy of the gamma-quantum, M the mass of the crystal, and c the velocity of light. It follows from this expression that the recoil energy is negligibly small and that the gamma-quantum carries with it all the energy of the isomeric transition.

The probability density $W(E)$ for the emission of a gamma-quantum with energy E is given by the equation

$$W(E) = \frac{1}{2\pi} \cdot \frac{\Gamma^2}{(E-E_0)^2 + \frac{1}{4}\Gamma^2},$$

where $\hbar/\tau = \Gamma$ is the width of the spectral line, and τ is the lifetime of the excited nucleus. The last equation thus describes the form of the nuclear spectral line.

Let us consider the following experiment. Let us assume that we have a source of monochromatic gamma-quanta (for example a ^{57m}Fe nucleus in stainless steel) which can move at a velocity of $\pm v$ relative to an absorber (^{57}Fe atoms in stainless steel). If the source is stationary, some of the gamma-quanta of the source, passing through the absorber, will be absorbed, and in accordance with the expression for $W(E)$, the absorption will be maximal. If however the source is moving relative to the absorber at a velocity $\pm v$, the energy of the gamma-quantum will be equal to

$$E = E_0 \pm E_0 \cdot \frac{v}{c}$$

and the absorption will decrease. The dependence of the count rate behind the resonance absorber on the velocity of the source relative to the absorber is called the Mössbauer spectrum.

Up to the present we have considered a radiating atom rigidly fixed in a crystal—the recoil energy is negligibly small, and all the gamma-quanta are "Mössbauer" quanta.

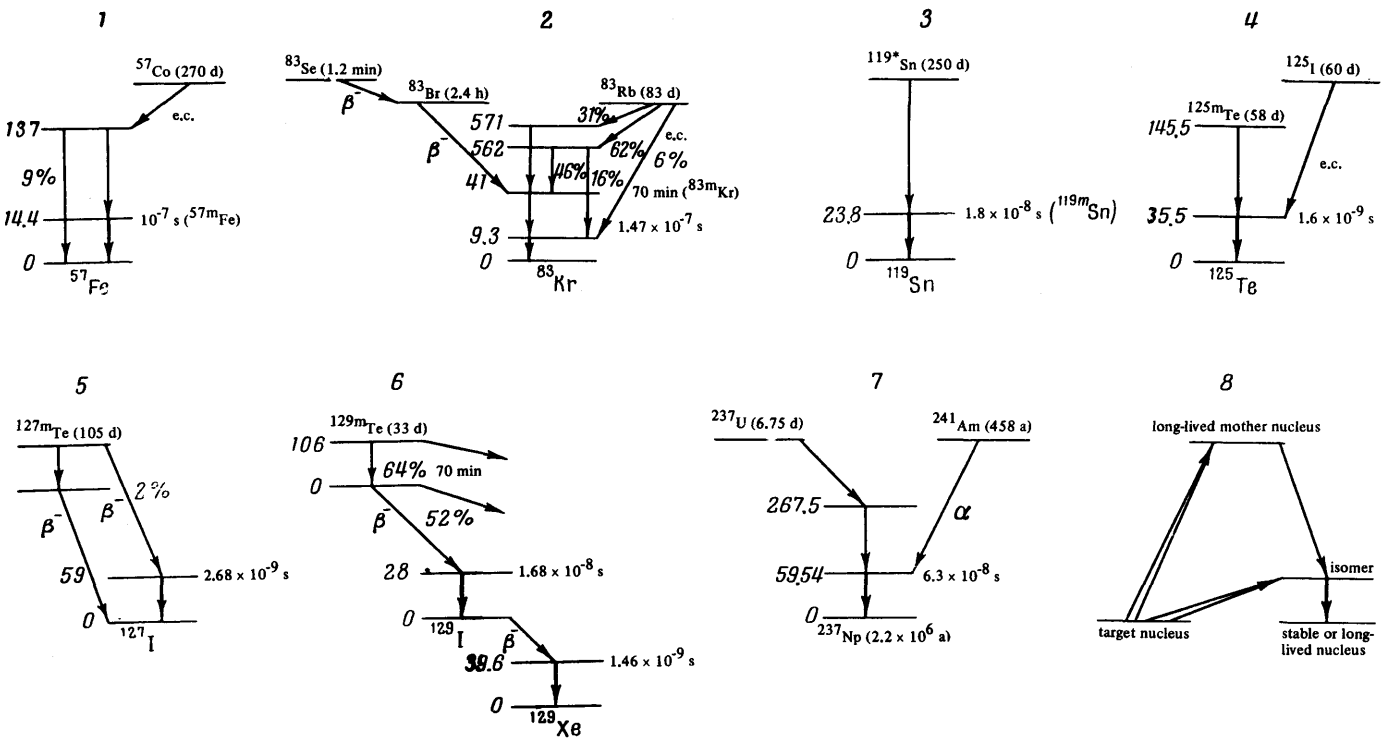


Figure 1. Decay processes leading to the formation of Mössbauer levels: *1*) ^{57}Fe; *2*) ^{83}Kr, *3*) ^{119}Sn, *4*) ^{125}Te, *5*) ^{127}I, *6*) ^{129}I and ^{129}Xe, *7*) ^{237}Np, *8*) general scheme for the formation of a Mössbauer level.

In a real example of gamma-quantum emission, however, the excitation of phonons of the crystal lattice is possible, leading to the partial loss of energy by the gamma-quantum, as a result of which the number of Mössbauer gamma-quanta decreases. The fraction of gamma-quanta emitted by non-phonon transitions is characterised by the quantity f—the Mössbauer coefficient. It is obvious that f characterises the "rigidity" of the lattice, and this coefficient will be small for atoms weakly bound to the matrix (for example, displaced from the normal lattice sites).

The energy of an isomeric transition depends on the electron density at the nucleus, so that for different compounds of the Mössbauer atoms the lines of the NGR spectra relative to a standard absorber (or source) will show a quite definite velocity shift, determined by the valency state (the so-called chemical shift). When the Mössbauer atom is in a distorted environment (different from cubic), the NGR spectrum shows quadrupole splitting, and finally when the M atom is introduced into a magnetic matrix, the phenomenon of Zeeman splitting of the spectrum is possible. Schemes for the formation and decay of various Mössbauer nuclei are given in Fig. 1.

III. THE INFLUENCE OF K-CAPTURE, ISOMERIC TRANSITION, AND β-DECAY ON THE FORMS OF STABILISATION OF A MÖSSBAUER ATOM

As a result of the removal of an electron from the K-shell (or L-, M-, etc. shells) in electron capture or a converted isomeric transition, a singly ionised excited atom is formed; this excitation is removed either by radiative transitions, leading to movement of the vacant position from the K-shell into the L-shell and then to the M-shell, etc., or by the emission of electrons (the Auger effect) leading to the accumulation of a high positive charge in the atom. Since there are a vast number of ways in which cascades of vacancies can develop, the final charge states of the atoms are not the same, that is a spectrum of charges is formed. The actual existence of multiply-charged ions when this process takes place in free atoms has been proved by mass spectrometry[5].

It is assumed that the accumulation of a large positive charge on an individual atom in a molecule produces forces of electrostatic repulsion, as a result of which the molecule dissociates, and the multiply-charged ion is in the "free" state[6]. The subsequent fate of this ion depends on the matrix in which the nuclear process takes place; within a definite time interval it reacts with the surrounding medium and is converted into stable forms (the forms of stabilisation).

There naturally arises the problem of the relaxation times of these highly charged metastable states of the atoms. If these times are much greater than the lifetime of the Mössbauer levels, the NGR emission spectra should contain lines corresponding to these states; if however these times are commensurate with the lifetimes of the Mössbauer levels, the spectra should show broadened lines.

An important feature of radiochemical theory is the assumption that the varied chemical forms obtained in a radiochemical analysis, for example in the study of an isomeric transition, are due to nuclear processes and can be only partly attributed to the influence of the subsequent chemical operations.

The process of β-decay (in the absence of a converted isomeric transition) does not lead to the formation of highly-charged ions, and the chemical changes accompanying β-decay are determined by the essential features of this process (the chemical behaviour of the daughter atom as distinct from the mother atom).

We can consider two basic problems:

1) what are the lifetimes of the metastable highly-charged states?

2) what are the forms in which Mössbauer atoms are stabilised?

1. LIFETIMES OF METASTABLE STATES

In the first moment after the formation of a Mössbauer level as a result of K-capture and an isomeric transition the atom is multiply-charged. It may be assumed that the law for the decay of these states (that is their conversion into the usual valency forms) obeys the exponential relationship[7]

$$I(n) = I_0(n) \exp\left(-\frac{\tau}{\theta(n)}\right),$$

where $I_0(n)$ is the intensity of the n-charged state in the initial moment after the formation of the Mössbauer level, τ the lifetime of the Mössbauer level, and $\theta(n)$ the lifetime of the n-charged state.

It is obvious that the metastable states, the lifetimes $\theta(n)$ of which are comparable with τ, should be revealed in the NGR spectra; the emission lines should be broadened, since[7]

$$\Gamma = \hbar\left[\frac{1}{\tau} + \frac{1}{\theta(n)}\right]$$

Thus the appearance of broadened lines in the emission NGR spectra may indicate that they belong to highly-charged states, the lifetimes of which are comparable with the lifetime of the Mössbauer level.

Electron capture in ^{57}Co has been most extensively studied in this connection. It was noted that if the decay of ^{57}Co takes place in a metal, the NGR spectrum always shows one line, corresponding to an Fe^0 atom (if the matrix is ferro- or antiferromagnetic, the spectrum will of course contain six lines). From this it may be concluded that in metals, in which there is a sufficient number of "free" electrons, the neutralisation of multiply-charged iron ions takes place in a time interval much smaller than 10^{-7} s.[3]

In semiconductors and dielectrics, however, which do not contain sufficient "free" electrons, the neutralisation possibly takes place much more slowly, so that the multiply-charged ions which have not decayed are revealed in the NGR spectrum by the production of a broadened line. This suggestion was put forward by Wertheim[8], when he found that the emission spectrum of cobalt oxide ^{57}CoO (at 295°K) contained two lines, one of which, from the chemical shift, corresponded to bivalent iron, whereas the second (slightly broadened) line corresponded to tervalent iron atoms (Fig. 2). Thus according to Wertheim, the multiply-charged iron ions in cobalt oxide are stabilised as Fe^{2+} (since CoO is isomorphous with FeO), and Fe^{3+} is a metastable form, which is converted into Fe^{2+} in a time interval of $\sim 10^{-7}$ s. More highly-charged states were not detected in the spectrum, and this led Wertheim to the conclusion that their lifetime is much less than 10^{-7} s. The spectra of cobalt oxide were subsequently studied by other workers[7,9-20], some of whom[7] also interpreted their results in terms of metastable states.

A large number of ionic salts of cobalt and iron labelled with ^{57}Co have been studied[13,14,19,21-25]. The studies of the iron salts are of greatest interest, since in this instance it is possible to study both emission and absorption NGR spectra in a single specimen. The two spectra for

$[Fe(NH_4)_2(SO_4)_2.6H_2O]$: ^{57}Co (Fig. 3) show that the absorption spectrum corresponds to only bivalent iron, whereas the emission spectrum shows a characteristic distortion, assigned[23] to the presence of metastable tervalent iron. The emission spectrum of $^{57}CoSO_4.7H_2O$ was interpreted analogously[24]. Finally, the spectrum of $^{57}Co(NH_4)_2(SO_4)_2.6H_2O$, in addition to bivalent and metastable tervalent iron, also showed metastable quadrivalent iron[23].

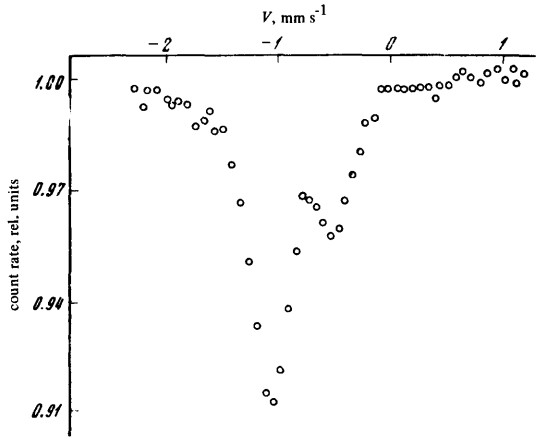


Figure 2. NGR spectrum of ^{57}CoO. Absorber—stainless steel[20].

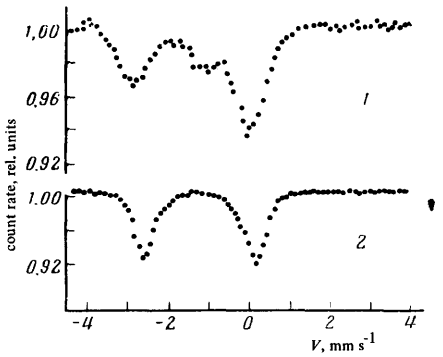


Figure 3. Emission spectrum of $[Fe(NH_4)_2(SO_4)_2.6H_2O]$: ^{57}Co (*1*) and absorption spectrum of $[Fe(NH_4)_2(SO_4)_2.6H_2O]$ (*2*).[14].

While referring the reader to the original papers[7-25] for details, we would point out that the only proof of the production of metastable states after the decay of ^{57}Co is provided by the broadening of the corresponding lines in the NGR spectra. The broadening may, however, be due to some other phenomenon (see below), so that in general, independent experiments which would determine directly the lifetime of these metastable ions are required. Studies of this kind were made by Triftshauser and Craig[12,14,21] for a large number of compounds of cobalt and iron, labelled with ^{57}Co. These involved essentially the application of the method of delayed coincidence; they recorded the gamma-quanta emitted by ^{57m}Fe nuclei in the time intervals (4–43), (43–86), (86–146), and (146–200) ns after the formation of the Mössbauer level (the moment of formation of ^{57m}Fe was recorded by detecting the 122 keV gamma-quantum—see Fig. 1). For the "ordinary" spectrum of ^{57}CoO, recorded without a delay, the authors cited[12,21] obtained $I(+3)/I(+2) \simeq 0.6$ (here $I(+3)$ and $I(+2)$ are the intensities of the Fe^{2+} and Fe^{3+} lines in the spectrum). If it is assumed that tervalent iron is metastable, this ratio should be different for different delay times[26]. It was found[12,21], however, that the ratio $I(+3)/I(+2)$ is independent of the delay time. Analogous results were also obtained for the systems NiO : ^{57}Co, $[Fe(NH_4)_2(SO_4)_2.6H_2O]$: ^{57}Co, $^{57}CoSO_4.7H_2O$, and $^{57}CoCl_2.2H_2O$.[12,14,21]. In other words, the tervalent iron ions formed after the decay of ^{57}Co are also stable, and the time required for the stabilisation of the multiply-charged states of the iron atoms is much less than 10^{-7} s.

Highly charged metastable states similarly were not observed in the formation of other Mössbauer levels (for example for the isomeric transition in ^{119}Sn). It may be concluded with a high degree of reliability that the relaxation times of highly-charged states in solids are much shorter than the lifetimes of the Mössbauer levels (10^{-7}–10^{-9} s).

2. FORMS OF STABILISATION OF MÖSSBAUER ATOMS

a. Electron Capture

It has already been noted that for the decay of ^{57}Co in metals, the NGR spectra in non-magnetic matrices consist of single lines with a chemical shift close to that for Fe^0. This is to be expected, since metals contain sufficient free electrons.

Similarly, in compounds of bivalent iron and cobalt labelled with ^{57}Co we should expect the formation of Fe^{2+}. In fact, in $CoCl_2$, iron is stabilised[13,23,27,28] only in the form of Fe^{2+}, but in $CoCl_2.nH_2O$ (n = 2, 4, or 6) the spectra show characteristic distortion, attributed[23] to the production of tervalent iron ions. Analogous distortions in the NGR spectra of $CoSO_4.7H_2O$, $CoSO_4$, $Co(NH_4)_2(SO_4)_2.6H_2O$, and $[Fe(NH_4)_2(SO_4)_2.6H_2O]$: ^{57}Co were also attributed to the production of tervalent iron[14,23,24], and this may be related to distortion of the structure of the crystal lattice[14] in the environment of the ^{57}Co atom.

An interesting explanation of the distortion of the spectra of $CoCl_2.nH_2O$ was put forward by workers[13] who studied the dependence of the form of these spectra on the quantity of hydrate water in the compound (n = 0, 2, 4, 6) and concluded that the spectrum of $CoCl_2.2H_2O$ consists of the superposition of the spectra of $CoCl_2$ and $CoCl_2.2H_2O$, that is that the distortion of the spectrum is due to the formation of different hydrates of $CoCl_2$.

A large number of studies have been made of the emission spectra of ^{57}Co in various matrices: Co_3O_4, Co_2O_3,[19,20,29,30] NiO,[31-35] MgO,[34-38] MnO,[34,35] CaO,[37,38] CaF_2,[39] $SrTiO_3$,[40] NaF,[22] NaCl,[27,41] AgHal,[42-48] KCl,[49] semiconducting compounds[50-56], and organic compounds of cobalt[57,58]. None of these papers reported the appearance, in the Mössbauer spectra, of lines related to charged states of iron, which would not have been characteristic of the chemistry of iron.

It may be noted that for CoO the production of a tervalent iron line has not yet been fully explained: some

authors [12,14] consider that this is due to the non-stoichiometry of cobalt oxide, whereas others [13,15] suggest that there exist two forms of cobalt oxide—CoO^{I}, in which iron is stabilised in the form of Fe^{2+}, and CoO^{II}, in which Fe^{3+} is stable (for a continuation of the discussion, see Refs. 17, 18, and 59).

K-capture in the case of ^{125}I in copper [60,61] produces in the NGR spectrum only lines corresponding to Te^{0}. For $NaIO_3$, distortion of the spectrum was observed, and this was attributed [60] to the formation of two charged states of tellurium.

Thus the process of K-capture in a solid leads to a limited number of forms of stabilisation of the Mössbauer atom. A characteristic feature of the NGR spectra is their broadening (for example the broadening of the line for tervalent iron in the emission spectrum of cobalt oxide), which apparently indicates a slight difference in the environment of each individual atom.

b. Isomeric Transition

The multiply-charged ions of ^{119m}Sn produced in the conversion of 65.3 keV gamma-quanta in metals and intermetallic compounds are stabilised, as expected, in the form of Sn^{0}. It is obvious that in quadrivalent tin compounds the tin atoms should be stabilised in the form of Sn^{IV}, and this is observed experimentally (for example, tin(IV) oxide, calcium and barium stannates). The situation is more complex for bivalent tin compounds, in which the expected form of stabilisation of the Mössbauer atoms is Sn^{II}. For example, it was found [62] that the emission spectrum of Sn^{II} oxalate shows a bivalent tin doublet, but it was found to be broadened relative to the absorption spectrum of the oxalate, and the magnitude of the effect was smaller; in the opinion of the authors cited, this was due to the existence of some of the ^{119m}Sn atoms in a locally distorted environment. This local distortion may be the result of a strongly converted isomeric transition preceding the Mössbauer transition.

An analogous picture of broadening of the emission spectra of ^{83}Kr has been observed [63-69]. In fact, most mother nuclei of krypton (^{83}Rb, ^{83}Br, and ^{83}Se) decay with the formation of ^{83m}Kr (half-life 70 min). After the converted 31.7 keV gamma-transition, a strongly ionised Mössbauer atom is formed. It is this process which leads to breakdown of the charge symmetry of the ligands and broadening of the ^{83}Kr spectra in dielectrics [66,68]. It was reasonable to assume that processes involving the relaxation of these distortions should take place much more intensively in semiconductors and metals than in dielectrics, and the emission spectra of krypton in this case will have narrow lines. This suggestion has been confirmed [68] (see Table 1).

The isomeric transition in ^{125m}Te in PbTe, metallic tellurium, amorphous tellurium, and tellurium dioxide does not give a set of valency states in the NGR spectra [70,71]. The hydrated compounds H_6TeO_6 and $Na_2H_4TeO_6$, however, show distortions of the spectra†, which were interpreted [71] as due to the production of Te^{IV} atoms together with Te^{VI}. It may be noted that this is not the only possible interpretation, since by analogy with hydrated compounds of cobalt the distortions of the spectra of these compounds may also be due to the formation of a set of Te^{IV} [Te^{VI}? (Ed. of Translation)] with different concentrations of hydrate water.

Thus although the metastable multiply-charged atoms formed after a nuclear transformation are stabilised fairly rapidly (at least in a time interval much shorter than 10^{-7}–10^{-9} s), local distortion of the lattice (as a consequence of the nuclear process) causes each individual atom to have an environment differing slightly from that of the other atoms, and this is responsible for the broadening of the NGR emission spectra and the small magnitude of the effect. It is therefore possible that on dissolution, the atoms which have undergone a nuclear transformation in the solid and have essentially identical chemical character will be distributed in different chemical forms (because of the influence of the nature of the local environment of the recoil atom) in the dissolution process, although the NGR spectrum may correspond to only one state.

Table 1.

Source	Source line width, mm s^{-1}	References
Kr (clathrate)	0.61	66
LiBr	0.65	
KBr	0.75	
NH_4Br	0.87	
$KBrO_3$	1.60	
RbCl	0.70	67
$RbClO_4$	0.85	
ZnSe	0.13	68
PbSe	0.13	

c. β-Decay

The influence of β-decay on the charge states of Mössbauer atoms has been studied for the example of ^{129}I ($^{129}I \xrightarrow{\beta^-} {}^{129m}Xe$). [72-75] It was found that the sources KIO_4 and $Na_3H_2IO_6$ give one line, so that the following compounds are apparently formed:

$$IO_4^- \xrightarrow{\beta^-} XeO_4, \quad IO_6^{5-} \xrightarrow{\beta^-} (XeO_6)^{4-}$$

The β-decay of ^{129}I in $NaIO_3$, $KICl_4.H_2O$, and $KICl_2.H_2O$ gives XeO_3, $XeCl_4$, and $XeCl_2$ respectively; the emission spectra of these products coincide with the absorption spectra. No additional lines were detected (it may be noted that the lifetime of ^{129m}Xe is $\sim 1.5 \times 10^{-9}$ s).

The influence of the β-decay of ^{129}Te on the charge states of ^{129}I has been studied [76-80]. ZnTe, [76-79] tellurium, tellurium dioxide, $Te(NO_3)_4$, [78] and magnesium, calcium, strontium, and barium orthotellurates [80] give spectra corresponding to the existence of one charge state of ^{129}I.

Slightly different results were obtained in a study of the β-decay of ^{127}Te. In ZnTe and tellurium, one charge state of the iodine atoms was detected [76,81-83], whereas in H_6TeO_6 one broad line was obtained; this was attributed [83] to the formation of other products in addition to IO_6^{5-}. It may be noted that for the orthotellurates of the alkaline earth metals (^{129}I NGR) it was found [80] that the width of the spectra depends on the history of the specimens and cannot be attributed to the production of a set of chemical forms of iodine. In this instance [83] the broadening of the spectrum of H_6TeO_6 may be similar in character.

† By distortion of the emission NGR spectrum, we mean a difference between its parameters or form and those of the corresponding absorption spectrum.

Thus emission Mössbauer spectroscopy indicates fairly unambiguously that daughter atoms are stabilised in a time interval much smaller than 10^{-9} s, in an extremely limited set of chemical forms and valencies. The chief role in the production of the large number of chemical forms frequently detected in radiochemical analysis is played by the dissolution process.

IV. PROCESSES OF ENERGY LOSS BY RECOIL ATOMS IN SOLIDS

To describe the chemical behaviour of highly energetic recoil atoms in a solid, models incorporating the results of the radiochemical analysis of irradiated systems and the theories of the mechanisms of energy loss by a "hot atom", developed in solid state physics, are being developed. In was noted in the introduction that the study of "hot" atoms or "recoil" atoms was based on the discovery of Szilard and Chalmers. These historically developed names are explained by the fact that the atoms produced in a nuclear reaction, as a consequence of the law of preservation of momentum, have a recoil energy which is much greater than the energy of the chemical bonding of the atom in the original molecule. Rupture of the chemical bond and decomposition of the mother molecule are thus unavoidable. In the study of the chemical effects of nuclear reactions by radiochemical methods, however, it is often necessary to assume high retention values (up to 100%). Thus it is obvious that the problem of the behaviour of so-called "hot" atoms—the loss of their excess of energy and the interaction with the environment—is a central problem in the study of the chemical consequences of nuclear reactions.

We may note several criteria by means of which radiochemists can judge the value of the theories developed in this field: 1) the ability of the model to give information on the nature of the primary products, that is the changes produced by the recoil atom in its original environment (we have in mind changes in the chemical, electronic, and three-dimensional structures); 2) its ability to reflect the influence of the crystal lattice parameters (that is the individuality of the chemical compound) on the nature of the changes produced; and 3) the ability of the model to establish the relationship between the picture of the changes in the solid and the picture of the distribution of the radioisotope among the different chemical forms in solution.

It should immediately be said that no single theory satisfying these criteria to a sufficient degree has yet been developed in radiochemistry and nuclear chemistry.

The phenomena of "retention" (that is the existence of radioactive atoms in the mother form) and "yield" (that is the existence of radioactive atoms in chemical forms differing from the mother form) are explained in radiochemistry by means of models of various kinds, proposing different mechanisms for the interaction of a hot atom with the environment in a crystal lattice. The principal models of the process of energy loss by recoil atoms have been described in detail[1].

In the "billiard ball" model, the hot atom loses the recoil energy as a consequence of several elastic collisions with the atoms of the lattice. This leads to the idea of a molten region (with an original local temperature of 10^{-6}–10^{-7}°K) occupying a volume of $\sim 3 \times 10^5$ atoms and existing for about 10^{-8} s. We should expect that partial mixing of the substance in the molten zone would take place and that the distant environment would influence the chemical behaviour of the recoil atom.

The "ligand loss" model assumes the production of a series of charged fragments formed by a hot atom which has left its original environment (for example MnO_3^+, MnO_2^{3+}, MnO^{5+}, and Mn^{7+} in the (n,γ) reaction in potassium permanganate). Although the initial valency of the atom remains the same, the yields of the different chemical forms of the hot atom are attributed to the different reactions of the dissolving medium with the fragments produced in the solid.

The "hot zone" model, based on the theories of solid state physics on the movement of charged particles in a crystal lattice, leads, for example, to the following zone parameters for a recoil atom which has been stopped: for the typical example of an (n,γ) reaction, the volume of the region in the lattice heated above the melting point ($\sim$ 1000°K) corresponds to $\sim$ 1000 atoms, and the lifetime of this "hot zone" is $\sim 10^{-11}$ s. It is suggested that the fusion region consists of a superheated solid rather than a melt, although genuine fusion is possible at its centre.

Thus these models indicate the existence of significant collective changes in the region of the arrested hot atom (significant changes in the chemical, electronic, and three-dimensional structures of the environment). According to these models, which are used to explain the variety of chemical forms produced by recoil atoms, the chemical bonding in the original molecule is generally broken, the hot atom is in the "free" state, and in the final analysis its environment is different from that in the mother matrix.

The values of the retention obtained by radiochemical analysis can be explained only by introducing different mechanisms for the conversion of the recoil atoms into the form of the original compound. Four forms of retention are usually considered[6]: preservation of the original bonds in the molecule in the nuclear process—a comparatively rare situation (primary retention), and return to the original chemical form as a result of: reactions of the "hot" atoms by a mechanism of elastic collisions and epithermal reactions of the radioactive atoms (secondary retention), reactions of radiation-chemical synthesis (tertiary retention), and finally thermal reactions of the recoil atoms and processes of thermal isotopic exchange (quaternary retention).

It is obvious that emission Mössbauer spectroscopy (when the Mössbauer transition is a direct consequence of a nuclear reaction in the solid phase) can be used to verify some of the assumptions of these models. Thus the existence of a melt in the zone of the recoil atoms (for the "billiard ball" model) with a lifetime of 10^{-8} s should make it impossible to observe the NGR emission spectrum. If the "ligand loss" or "hot zone" models are realised, extremely significant changes in the spectra are unavoidable, due to the fact that only a very small number of recoil atoms are in a truly initial "mother" environment after 10^{-7}–10^{-9} s. In this instance the part of the emission spectrum corresponding to the mother chemical form of the Mössbauer atom in the solid (that is the retention) can be produced only by the recoil atoms which have been preserved in this form by a primary retention mechanism ("the rare case of preservation of the original bonds in the molecule") and by the mechanism of epithermal reactions of the radioactive atoms. Tertiary and quaternary retention cannot contribute to the total retention when the Mössbauer experiment is carried out directly "under the beam" (for example, excitation of the ^{57m}Fe level as a result of (d,p) and (n,γ) reactions and Coulombic excitation). Secondary retention by the mechanism of "hot" atom reactions, as shown above, similarly cannot contribute to the total retention because of the existence of a molten region

in the zone of the recoil atom at the moment of emission of the resonance gamma-quantum.

It is clear that the experimental observation of the Mössbauer effect after a nuclear reaction makes it possible to follow the fate of highly energetic recoil atoms. The actual existence of NGR spectra, and also their parameters, obviously make it possible to discuss the substance of various models of the process of energy loss by hot atoms in a crystal lattice.

1. USE OF THE MÖSSBAUER METHOD TO STUDY PROCESSES OF ENERGY LOSS BY HOT ATOMS

a. Metallic Targets

Coulombic excitation of the ^{57m}Fe level by α-particles with energy 3 MeV in a target of magnetic iron [84-87] did not show a decrease in the Mössbauer coefficient f for the target relative to f for ^{57}Co, introduced by diffusion into stainless steel (the difference was not greater than 5%). Similarly, differences were not observed in the chemical shift and fine magnetic structure of the Mössbauer spectra of the two sources.

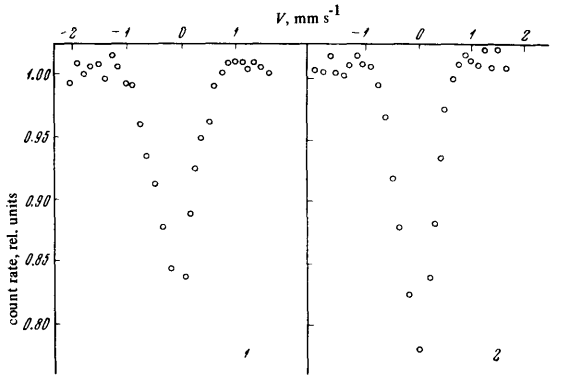


Figure 4. NGR spectrum from a source obtained by the (d,p) reaction in non-magnetic iron (*1*) and from a source obtained by the introduction of ^{57}Co into non-magnetic iron by diffusion (*2*). The background was not taken into account. Absorber—stainless steel [94].

A unique method of Coulombic excitation of the ^{57m}Fe level was used by Sprouse and coworkers [88]: the ^{57m}Fe atoms ejected from a stainless steel target by oxygen ions with energy 36 MeV were passed through a vacuum on to a support of copper, aluminium, gold, or magnetic iron, which thus acted as Mössbauer sources. Comparison of the spectra obtained in this way with the spectra of ^{57}Co introduced into the same matrices showed that the two types of spectra are identical.

It may be concluded that in metals, the atoms which have undergone Coulombic excitation are in the lattice sites for a time interval much smaller than 10^{-7} s, and that their environment does not differ from the environment in the ordinary lattices (otherwise, the magnitude of the effect would decrease, a chemical shift would be observed, and the internal magnetic field acting on the iron nucleus would change). This conclusion is confirmed by analogous results obtained for the Coulombic excitation of the Mössbauer level of ^{61}Ni [89] and the Mössbauer levels of the rare earth elements in metallic targets [90-92]. Thus a metallic ^{184}Yb target has been used as source [91], the metal also acting as absorber. The Mössbauer spectrum consisted of a singlet line, the width of which was greater than that of the natural line by a factor of only 1.3. The magnitude of the effect was $f_{expt} \simeq 0.05 \pm 0.03$, whereas $f_{theor} = 0.08$. All this led to the suggestion [91] that radiation changes do not take place close to the Mössbauer atom. It should be remembered that the recoil energy for Coulombic excitation may reach 100 keV.

The reaction ^{56}Fe$(d,p)^{57m}$Fe in metallic iron has been studied [93-95] (recoil energy ~ 500 keV). The NGR spectra for ^{57m}Fe, obtained by the (d,p) reaction in non-magnetic iron, and for ^{57}Co introduced by diffusion into the same matrix [94] are given in Fig. 4. The results of the treatment of these spectra are given in Table 2.

Table 2.

Parameters of the spectra	Source	
	^{56}Fe$(d,p)^{57m}$Fe	^{57}Co
Chemical shift, mm s^{-1}	0.00	0.00
Amplitude of effect, %	31±4	29±2
Width, mm s^{-1}	0.37±0.04	0.36±0.04

For the ^{57m}Fe source obtained by the (d,p) reaction, a chemical shift relative to the ^{57}Co source in the same matrix is not observed (Table 2). The magnitude of the effect and the width of the line in the spectrum remain unchanged.

For a magnetic iron target, the (d,p) reaction similarly does not lead to a decrease in the effect or to a change in the fine magnetic structure of the NGR spectrum [93-95].

The temperature of the local environment of the ^{57m}Fe recoil atom formed in the (d,p) reaction in magnetic iron was determined [95] from the temperature dependence of the magnitude of the magnetic splitting of the spectrum. In the range of target temperatures between −195° and +40°, the temperature of the environment of the recoil atom was found to be equal to the macro-temperature of the target.

Thus in the (d,p) reaction in a metal lattice, as in the Coulombic excitation examined above, the recoil atoms are produced in a time interval much less than 10^{-7} s, in normal lattice sites, and the temperature of their environment is equal to the macro-temperature. It is obvious that the formation of a molten zone and turbulent mixing of the substance in the recoil zone would have led unavoidably to significant changes in the NGR spectra, but this was not observed experimentally.

The reaction ^{56}Fe$(n,\gamma)^{57m}$Fe in metallic magnetic iron was also studied by the NGR method [96]. The spectrum obtained was the same as the spectrum of ^{57}Co in an analogous matrix, indicating that the ^{57m}Fe atoms after the (n,γ) reaction under the beam (recoil energy $\leq$ 540 eV) are in normal lattice sites. The (n,γ) reaction, carried out under a neutron beam for ^{155}Gd and ^{157}Gd [97] and for ^{39}K [98,99] in metallic targets similarly does not lead to the production of displaced Mössbauer atoms.

b. Non-metallic Targets

Experiments on the study of various nuclear reactions by the NGR method in non-metallic targets are of the greatest interest for the solution of chemical problems of the behaviour of hot atoms in solids.

The Coulombic excitation of the ^{57m}Fe level in Fe_2O_3 showed a decrease in the quantity f for this source relative to f for the source Fe_2O_3 : ^{57}Co. [85-87] The fine structure of the spectrum of the Fe_2O_3 target remains unchanged, as does the chemical shift. The authors cited [85-87] suggest that some of the ^{57m}Fe recoil atoms, after Coulombic excitation, are displaced from the normal lattice sites, leading to a decrease in f. There are no grounds for assuming the possibility of the production of molten zones on energy loss by the hot atom; if this were the case, the NGR spectrum would show a change in fine structure and a chemical shift.

Analogous results were obtained for the Coulombic excitation of the Mössbauer level in ^{73}Ge. [100-102] The decrease in f for the target cannot be attributed to the existence of a hot zone, since the width of the spectrum would have increased [101].

Coulombic excitation of the ^{174}Yb Mössbauer level in Yb_2O_3 [91] gave a spectrum identical to the absorption spectrum of Yb_2O_3. The authors cited [91] concluded that the greater part of the ^{174}Yb atoms after the Coulombic excitation remain in the lattice sites.

The $^{56}Fe(d,p)^{57m}Fe$ reaction in non-metallic targets leads to a decrease in f relative to f for ^{57}Co in the same matrices [95].

The $^{56}Fe(n,\gamma)^{57m}Fe$ reaction in Fe_2O_3 and $FeSO_4.7H_2O$ led to a slight change in the NGR spectra of these targets relative to the spectrum of ^{57}Co in Fe_2O_3 and the absorption spectrum of $FeSO_4.7H_2O$. For Fe_2O_3, a slight decrease in the effective magnetic field acting on the iron nucleus was observed, and for $FeSO_4.7H_2O$ a line characteristic of tervalent iron appeared [96]. This indicated the production of displaced atoms in the targets; for $FeSO_4.7H_2O$, these atoms may also be stabilised in the form of Fe^{3+}.

It should be emphasised that even in such complex compounds as Fe_2O_3 and $FeSO_4.7H_2O$, a considerable proportion of the recoil atoms remain in the normal lattice sites, that is their environment after the (n,γ) reaction is the same as the original environment.

In a study of the (n,γ) reaction under a neutron beam for ^{157}Gd and ^{155}Gd isotopes by the NGR method, it was established that in oxide targets (unlike metallic targets) a slight change in the spectrum is observed; a possible reason for this is that some of the recoil atoms are in displaced positions [97].

It has been shown [98] that, for example, for a source in the form of a KCl target [the reaction $^{39}K(n,\gamma)^{40}K$] the magnitude of the effect is close to the theoretical (f_{expt} = 0.11 ± 0.02, f_{theor} = 0.12 at 80°K), and the width of the spectrum differs little from the theoretical. This may confirm that in the reaction $^{39}K(n,\gamma)^{40}K$ in KCl, the greater part of the potassium atoms at the moment of emission of the Mössbauer gamma-quantum ($\tau \simeq 4 \times 10^{-9}$ s) are in lattice sites. It may be noted that the recoil energy in this case reaches 800 eV.

Various complex compounds of potassium, for example $KAlSi_3O_8$, have been used as targets for irradiation by neutrons [99], but all the spectra consisted of a single line, the width of which exceeded the natural width by a factor of not more than 1.3. This indicates again that there are no significant radiation changes in the environment of an atom which has undergone an (n,γ) reaction.

The $^{118}Sn(n,\gamma)^{119m}Sn$ reaction in tin oxide under conditions of prolonged reactor irradiation has been studied [62,103]. It was found that the spectrum of irradiated ^{118}SnO, in addition to the Sn^{II} doublet, contained a weak Sn^{IV} line. The spectrum of the same specimen, dissolved in hydrochloric acid and frozen, showed a marked increase in the intensity of the Sn^{IV} line (Fig. 5). This is apparently related to the fact that in the (n,γ) reaction under the conditions of prolonged irradiation in a reactor, some of the recoil atoms are displaced, and the intensity of the line from these tin atoms is slight when the spectrum is dissolved. All the radiating atoms are in identical conditions, and this leads to an increase in the intensity of the Sn^{IV} line.

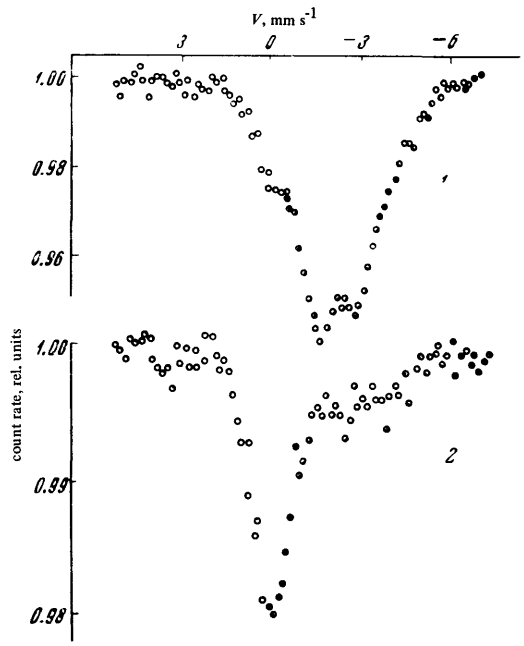


Figure 5. NGR spectra of ^{118}SnO, irradiated in a reactor, at 80° K (*1*) and a hydrochloric acid solution of the same specimen at 80°K (*2*). Absorber—calcium stannate [62].

Slightly different results were obtained for the reactor irradiation of ^{118}SnO and $^{118}SnO_2$, [104] when complex NGR spectra were obtained. The results were interpreted in terms of the "hot" zone model. Later work [62], however, did not confirm these results.

Interesting results were obtained in a study of α-decay in ^{241}Am. [105-111] The spectrum of $^{241}AmO_2$ in NpO_2, and for comparison the spectrum of $^{237}UO_2$ in NpO_2 (the β-decay of ^{237}U gives the same Mössbauer level ^{237}Np), [105] are given in Fig. 6. It can be seen that the effect is much smaller for α-decay than for β-decay. Since the recoil energy after the α-decay of ^{241}Am is ~ 93 keV, displacement of some of the daughter atoms from normal crystal lattice sites is possible, and this decreases the value of f. The theory of the Mössbauer effect after α-decay has been developed [112] and it has been shown that relaxation processes may be responsible for the broadening of the line.

Thus the existence of emission Mössbauer spectra after nuclear reactions characterised by high recoil energies [Coulombic excitation, α-decay, (d,p), and (n,γ)] clearly indicates that a considerable proportion of the recoil atoms, at the moment of emission of the resonance gamma-quanta, are in normal lattice sites. The existence of molten regions, mixing of the substance, and the production of significant radiation damage in the region of the recoil atom are not confirmed. It of course follows from these spectra that some of the recoil atoms after the nuclear reaction are in a local environment which is different from the mother environment, and this is revealed by broadening of the lines and a decrease in the effect.

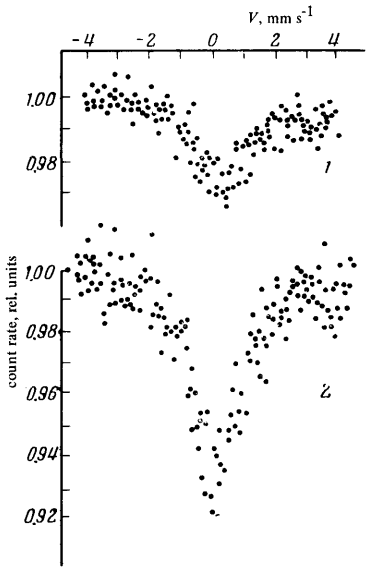


Figure 6. NGR spectra of $^{241}AmO_2$ (*1*) and $^{237}UO_2$ (*2*). Absorber—NpO_2.[105]

The next paragraph describes briefly studies carried out in the last ten years in the field of the physics and chemistry of the solid state, the essential feature of which is the departure from models based on a description of significant changes in the region of the arrested hot atom.

2. PRESENT IDEAS ON PROCESSES OF ENERGY LOSS BY RECOIL ATOMS

We shall try to follow the analogy in the results of the following studies: 1) the solution of the problem from the equilibrium and dynamics of the formation of defects in the crystal lattice; 2) the determination of the parameters of the reaction zone of the recoil atom by radiochemical experiments; and 3) the study of chemical effects in crystals bombarded with accelerated ions.

About ten years ago, theories of so-called crowdions and focusons—new mechanisms of the transfer of atoms and the energy of atoms in crystals—were put forward[113-117]. These theories have been confirmed by calculations on electronic computers[118,119] and by comparison of the results with experiment.

Among the many conclusions following from these calculations, the following is of particular interest: the propagation of the energy of the primary atom in the crystal does not produce phenomena resembling fusion or the turbulent mixing of atoms. Calculations for the recoil energy characteristic of the (n,γ) reaction do not confirm the existence of high temperatures, continuation of the existence of a hot zone, or the collective nature of the changes.

To verify these ideas regarding the dynamics of radiation damage, radiochemical experiments were carried out to determine the parameters of the reaction zone of the recoil atom [the (n,γ) reaction].[120-124] The homogeneous mixed crystals $K_2ReBr_6-K_2SnCl_6$; $K_2ReCl_6-K_2SnBr_6$; $K_2OsBr_6-K_2SnCl_6$; and $K_2ReBr_6-K_2OsCl_6$ were studied. The systems were irradiated with neutrons, and the products of the $^{185}Re(n,\gamma)^{186}Re$ reaction were determined quantitatively (by ionophoresis). For the $K_2ReBr_6-K_2SnCl_6$ system, for example, the K_2ReBr_6 concentration was varied in the range 1–28 mole %. The essential features of the experiments were as follows. The primary retention should be represented by the form of $ReBr_6^{2-}$ retained by the billiard ball mechanism at low concentration of K_2ReBr_6—in the form of $ReCl_6^{2-}$, and for retention by the hot zone mechanism we should expect a set of all forms of hexabromochlororuthenates $ReBr_{6-n}Cl_n^{2-}$ ($6 \geqslant n \geqslant 0$) with the conditions that the K_2ReBr_6 concentration is not too small.

Analysis of the results led to the following conclusions: 1) the billiard ball mechanism does not apply in any of the systems studied; 2) the concept of fusion in the reaction zone of the recoil atom is refuted, since otherwise the distribution of the yields of all possible bromochlororuthenates should have been close to the random distribution, and this is not observed; and 3) the region of the reaction zone of the recoil atom is smaller and broken down to a smaller extent than is assumed in the hot zone model; fusion processes and significant turbulent mixing of the atoms do not take place in the reaction zone.

Let us now consider experiments on the study of chemical reactions with accelerated ions[125]. These experiments make it possible to compare the results for the chemical distribution of ^{51}Cr atoms in different compounds of chromium subjected to bombardment by accelerated $^{51}Cr^+$ ions or irradiated with thermal neutrons. The results[125] show that the same radioactive products are obtained on dissolution of the crystals after both experiments, and also that a similarity is observed in the kinetics of formation of the $^{51}CrO_4^{2-}$ fragments on thermal annealing (that is complete similarity in the processes of increase in retention on annealing in the two experiments). In the opinion of the authors cited[125], this similarity confirms the hypothesis that the changes in the valency state of radioactive atoms on annealing reflect processes of electronic rearrangement in the crystal in the zone of the ^{51}Cr atom rather than restoration of the altered original molecule. It may be assumed that this conclusion confirms indirectly the theory that the changes produced by a recoil atom in a crystal lattice are small and purely local.

V. THE "SOLID–SOLUTION" PROBLEM

As already noted, one of the fundamental problems in the comparison of information obtained in the study of a solid and its solution is the determination of the influence of the solvent medium on the crystal. It is hoped that the use of the NGR method will provide new and promising possibilities in this connection. The use of other indirect methods to determine the nature of the environment of a recoil atom, not related to the dissolution procedure, is also of interest.

Promising possibilities are provided by the study of the angular correlation of cascade radiation as applied to the chemistry of hot atoms. Thus for $KReO_4$ crystals irradiated with neutrons, considerable breakdown of the angular correlation of the gamma-quanta of ^{188}Re was observed[126]. In the opinion of the authors cited, this indicates that irradiated $KReO_4$ contains forms of ^{188}Re different from the mother form. Nevertheless, chemical analysis of irradiated perrhenates shows 100% retention. This example appears sufficiently clear and demonstrates in this specific instance the "incompatibility" of information obtained before and after dissolution. An interesting feature is that the observed breakdown of the angular correlation to some extent agrees with the information obtained from emission Mössbauer spectroscopy, where the broadening of the lines and the decrease in the magnitude of the effect are attributed to the existence of some of the radiating Mössbauer atoms in an environment different from the mother environment.

In the comparison of the results obtained by the NGR method (and "physical" methods in general) and radiochemical results, allowance must also be made for possible changes in the initial distribution of the chemical forms of the hot atoms in the crystal, depending on the accumulated radiation dose, the extent of the defect character of the original specimens, the irradiation parameters, processes of thermal and radiation annealing, and a number of other factors.

Thus a study of the irradiation of $H_2TeO_4.0.36H_2O$ and H_2TeO_4 in a reactor established[127] that the yield of reduced forms of ^{131}I (the target was dissolved in aqueous KOH solution containing various iodine carriers) increases with increase in the integral neutron flux and the dose of accompanying gamma-radiation.

A study of the neutron irradiation of crystalline tellurium dioxide showed that the increase in the yield of reduced forms of ^{131}I is related to the effect of gamma-irradiation. It was proved[128] that the increase in the yield of reduced forms is due to the reduction of IO_3^- to I^- by reaction with elementary tellurium, formed by the gamma-irradiation of tellurium dioxide.

In the irradiation of $KSb(OH)_6.H_2O$ with thermal neutrons, the retention in the forms Sb^{3+} and Sb^{5+} depends on the quantity of water in the specimens[129].

From these examples it is clear that the borrowing of information from the radiochemistry of a given element for the interpretation of NGR spectra, and naturally the reverse borrowing, are in general inapplicable. Comparison of the results obtained by the two methods is desirable and allowable when the same specimens are studied, with detailed allowance for possible complicating features.

Examination of the information obtained by emission Mössbauer spectroscopy establishes some general features in the consequences of seven forms of nuclear transformation in solids [electron capture, isomeric transition, α-decay, β-decay, Coulombic excitation, and (n,γ) and (d,p) reactions].

1. The metastable highly-charged states of atoms produced as a consequence of nuclear transformations in a solid are discharged in a time interval much smaller than the lifetime of a Mössbauer level (10^{-7}–10^{-9} s) and are converted into stable forms characteristic of the macrochemistry of the given element.

2. The emission Mössbauer spectra generally correspond to an extremely limited set of forms of stabilisation of the recoil atoms (one or two), whereas the use of delicate analytical procedures in radiochemistry often reveals a rich spectrum of chemical forms and valencies. This "discrepancy" is apparently related to the influence of the local environment of the recoil atom (revealed in the emission NGR spectra by broadening of the lines and a decrease in the magnitude of the effect) on the distribution of the radioisotope being studied among different chemical forms during dissolution.

3. The study of the processes of energy loss by hot atoms by Mössbauer spectroscopy does not show the existence of molten zones and mixing of the substance in the reaction region of a highly energetic recoil atom. Even in comparatively complex compounds at high recoil energies, a considerable proportion of the Mössbauer atoms at the moment of emission of the resonance gamma-quantum are in the normal sites of the crystal lattice, and their environment does not differ from the original environment.

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In the two years since the review was written, a large number of papers on the use of the Mössbauer effect to study the after-effects of nuclear transformations in solids have been published. Of work by Soviet authors, mention must first be made of the studies by Nesmeyanov and coworkers[130–132], who investigated the influence of the converted isomeric transition in ^{125}Te and electron capture in ^{125}I on the chemical state of the daughter atoms. Anomalous charge states of Te were not detected, and stabilisation takes place in the usual forms of the macro-chemistry of this element.

The emission spectra of tin in alkali metal and silver halides have been studied[133,134]; no influence of the strongly converted isomeric transition in the 250-day isomer ^{119}Sn on the charge state of the daughter atoms was detected. Similarly, proof was not obtained for the existence of after-effects of electron capture in impurity ^{57}Co atoms introduced into the CoS lattice[135] and semiconducting compounds $A^{III}B^{V}$.[136] The problem of the influence of nuclear transformations on the chemical state of impurity tin and iron atoms in ionic crystals has been studied[137]. It is suggested that the absence of after-effects is related to the "rigidity" of the lattice of the matrices studied (a measure of this "rigidity" is provided by the Debye temperature). Murin and coworkers[138] assume as a working hypothesis that on obtaining recoil energy much greater than the energy of the bond formed by the atom in the lattice, a daughter atom may not leave the lattice site, because of breakdown of the correlation between the momentum and the energy of recoil.

Outstanding among work by authors in other countries is a paper[139] describing a detailed study of the influence of electron capture and β-decay on the chemical state of daughter atoms. The authors cited[139] consider that the changes in the local environment of atoms which have undergone a nuclear transformation (and hence the production of a large number of chemical forms of the daughter atoms) may be observed in lattices with low Debye temperatures or in lattices with a high concentration of defects (irrespective of the magnitude of the Debye temperature). It is suggested that stabilisation of the hot atoms leads to electronic structures characteristic of the macro-chemistry of the given element.

The problem of determining the lifetimes of the metastable states of ^{57m}Fe atoms formed after the decay of ^{57}Co in Cu_2O, MgO, and Al_2O_3 lattices has been studied[140]; it was shown that the iron atoms are stabilised in the usual valency states in time intervals much smaller than the lifetime of the Mössbauer level.

The Mössbauer effect has been studied for atoms which have undergone a nuclear reaction accompanied by a high recoil energy: the $^{56}Fe(n,\gamma)^{57}Fe$ reaction in metallic iron and Fe–Al alloys[141,142]; the α-decay of ^{241}Am;[14] and the Coulombic excitation of various nuclei[144-151]. Although the number of papers devoted to nuclear transformations accompanied by vast recoil energies is increasing rapidly, the problem of the behaviour of recoil atoms of this kind still remains a subject for discussion.

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