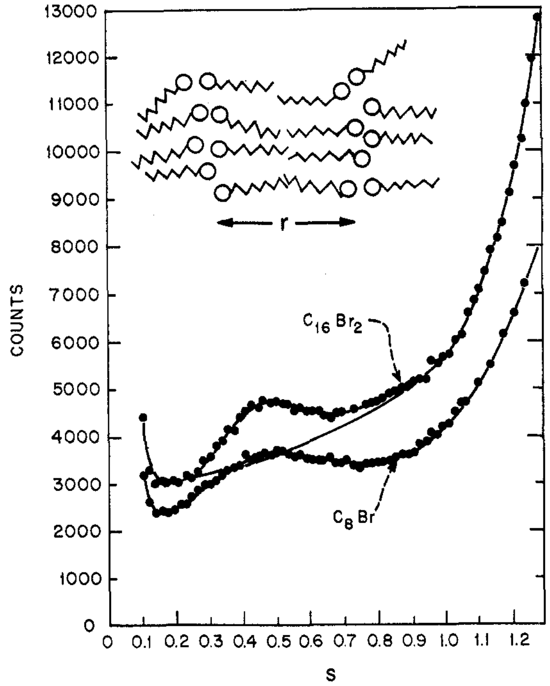

Figure 7. Intensity pattern of a dibromide, $C_{16}H_{32}Br_2$, and a monobromide, $C_8H_{17}Br$, of half the corresponding alkane chain length showing the existence of peaks in the intensity patterns at roughly the same angle. A crude model of the alignment is included. The circles are halogen atoms.

as solvent. A proper analysis of the data required a knowledge of the contributions to the intensity of the distribution functions of solvent and solute molecules with respect to themselves and each other. This could be obtained experimentally; in Figure 6, I_D, the function which measures the end-to-end I–I interaction, isolated from all the others, is shown. The full lines are the measured values and the dashed lines the calculated distribution. It is found that the width of the latter is ±2 Å and that the $\langle r_m \rangle$ values are in good agreement with those deduced by Flory from a rotational isomeric treatment. Full details are to be found in the original papers.[40,41]

A surprising result of the investigation[40] was the large amount of order present in the monoiodide solutions. This is illustrated in Figure 7, which shows a trace of the region of the intensity pattern of 1-bromooctane, where the corresponding 1,16-dibromohexadecane shows a peak. Clearly indicated is some type of quasi-liquid crystal behavior in which the long-chain molecules line up in such a way that the halogen atoms make maximum contact with each other, as do the chains themselves. We have established[42] the following. (1) The strong ordering tendency of the long-chain molecules persists when solvent is added. It becomes noticeably evident in the intensity pattern at concentrations of ~6 mole %. (2) In solutions of molecules of one chain length, C_mX, where X is a halogen, the peak occurs in the distance range corresponding to a length $\sim C_{2m}$. (3) In solutions of molecules of $C_mX + C_nX$, the distance range corresponds to C_{2m}, where m is the length of the longest chain. When the length C_m approaches the length C_n, the peak corresponds to a length C_{m+n}. Thus, a solution of C_2X and $C_{20}X$ alkanes gives a peak at $\sim C_{40}$. On the other hand, a $C_{10} + C_{12}$ solution exhibits a peak at C_{22} (10 + 12). (4) The peaks for the monosubstituted species are quite broad, while the α,ω-disubstituted compounds produce a relatively sharp peak characteristic of a well-defined distance.

In summary, by discussing sets of measurements on three different phenomena we have tried to present a brief representative survey of our work on small-angle scattering methods as applied to the liquid state.

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Chemical Effects of Nuclear Transformations in Mössbauer Spectroscopy

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Since its discovery[1] in 1958 the Mössbauer effect[2,3] has become an increasingly valuable spectroscopic technique.[4] It offers not only information comparable to that obtained from nuclear magnetic or nuclear quadrupole resonance but also unique ways of determining valence and studying covalency and lattice vibrations.

The effect is based on the resonant nuclear scattering of γ rays by atoms in solids. Only γ rays which have been emitted without recoil and therefore have the full energy of the nuclear transition can be resonantly scattered. The existence of such "recoil-free" γ rays can be understood in terms of the Debye–Waller factor, familiar from X-ray crystallography. They occur whenever the free atom recoil energy is smaller than the Debye energy, $k\theta_D$. Isotopes exist in which the majority of γ rays are emitted without recoil, making the Mössbauer effect a major one.

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The width of these γ rays is determined by the lifetime of the decaying nuclear state. For a number of isotopes it is $\sim$1 MHz, small enough that hyperfine perturbations of nuclear levels can be resolved.

Experiments are usually carried out in transmission geometry similar to that originally used by Mössbauer. A Doppler velocity is used to scan the energy of the γ ray. Carefully controlled Doppler velocities make it possible to map out the shape of the γ-ray line and to measure its shift and splitting. The relation of Doppler velocity, v, to energy shift, δE, is $\delta E/E = v/c$, where c is the velocity of light. Since E is large (10^4–10^5 eV) while δE is small (100 MHz $= 4 \times 10^{-7}$ eV), velocities of only a few centimeters per second are generally required.

The precise value of the energy of a Mössbauer γ-ray transition depends on the chemical environment of the emitting or absorbing nucleus. This manifests itself as a shift of the centroid of the Mössbauer effect absorption from zero Doppler velocity whenever source and absorber are chemically distinct. The shift arises from the electrostatic interaction of nuclear and electronic charges. In general, the effect is due to the s-electron charge density at the nucleus, $|\psi(0)|^2$, and to the difference between the mean square nuclear charge radii, $\delta\langle r^2\rangle$, of the isomeric excited and ground states. Because of this it is generally called isomer shift or sometimes chemical isomer shift, here abbreviated IS.

Isomer shifts provide information particularly useful to chemists because they are sensitive to valence and covalency, which affect s-electron charge density. They can even be used to identify the chemical state of an isolated impurity atom. It is this shift which has been most useful in identifying the new chemical species produced by the aftereffects of nuclear decay.

The decay of a radioactive atom in a solid can have a wide variety of chemical consequences which are here collectively termed "aftereffects." The best known is the displacement of the atom from its lattice site by the recoil of the emission process. Equally well understood are effects arising from the ionizing properties of the emitted radiation.

A third, less well known, source of chemical effects is the so-called "Auger cascade." It is initiated by a nuclear decay event such as internal conversion or electron capture which removes a K-shell electron. The filling of this K-shell hole is accomplished in part by X-ray emission and in part by Auger effect. The latter is a two-electron, radiationless process in which one electron drops into the K-shell hole and the other is ejected from the atom. For atoms in low-pressure gases it has been shown that this leads to the production of highly ionized states. Various mechanisms have been proposed by which these highly charged "Auger cores" could produce chemical effects in the solid state.

The Mössbauer effect (ME) provides the ideal technique for the study of these questions because in many isotopes an energetic nuclear event precedes the emission of the ME γ ray. It is therefore possible to observe the chemical effect of the energetic event and even to obtain time-resolved information. ME measurements gave evidence for such chemical aftereffects within the first few years of the discovery of the effect, but detailed understanding is only now developing.

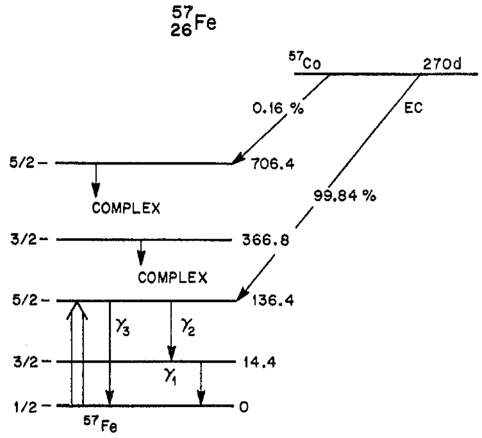

Figure 1. Decay scheme of ^{57}Co. The daughter, ^{57}Fe, is a stable isotope with a natural abundance of 2.17%. The Mössbauer γ ray is labeled γ_1.

Most of these experiments were carried out with ^{57}Fe, or rather with sources containing its radioactive parent, ^{57}Co, whose decay scheme is shown in Figure 1. The electron-capture decay of a cobalt nucleus produces an iron atom with a missing K electron. In 65% of the cases this hole is filled by the Auger effect, most likely with the emission of an electron with an energy of 5.4–5.7 keV and the creation of two L shell holes. These in turn are filled by further Auger events involving outer shells leading to a highly ionized atom on a time scale of $\sim 10^{-15}$ sec. The details of this Auger cascade have been described by Pollak.[5] The Auger cascade is followed by a prompt γ ray which populates the 14.4-keV level (half-life, 10^{-7} sec) which emits the ME γ ray. This γ ray then makes it possible to examine the aftereffects of preceding events on a time scale from 3×10^{-9} to 3×10^{-7} sec.

In general, one can predict that recoil effects will be too small to produce atomic displacements for this isotope. On the other hand, one can look for the effects of the ionization produced by the Auger electron and of the relaxation of the highly charged core produced by the Auger cascade. One can further anticipate that the observable effects will depend strongly on the nature of the host lattice. In metals the effects of ionization as well as the highly charged ion will disappear in the dielectric relaxation time. In insulators aftereffects may remain, but the details are not easily predicted.

Radiolysis in Hydrated Salts and Oxalates

A considerable effort has gone into the study of the chemical state of iron produced by the decay of divalent cobalt in various salts. It was soon recognized that hydrated salts are unique in always showing valence higher than those of the cobalt parent. Initially the additional finding of line broadening suggested a life-

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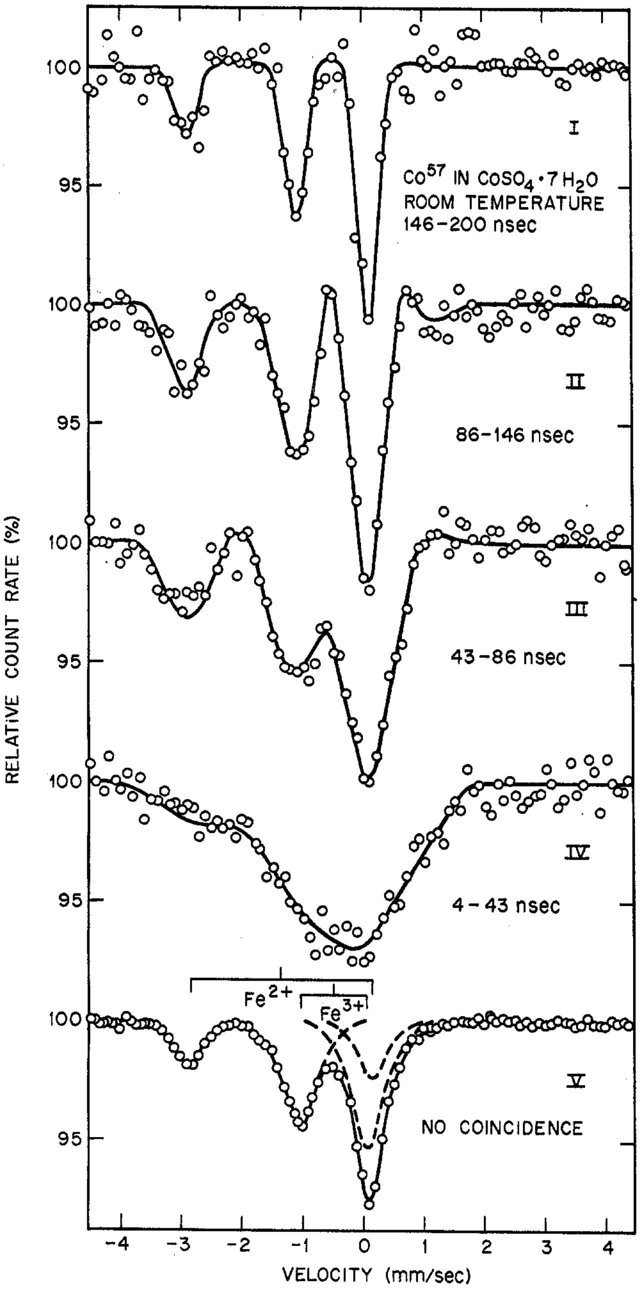

Figure 2. Time-resolved study of aftereffects in $CoSO_4 \cdot 7H_2O$. The ratio of Fe^{2+} to Fe^{3+} is the same for all decay times (from ref 7).

time effect, but the broadening has now been shown to arise from other causes.

There is currently good agreement on the production of Fe^{3+} by the decay of Co^{2+} in ferrous ammonium sulfate hexahydrate[6,7] and in various other cobalt compounds.[8-11] The role of the water of hydration has been directly examined by Friedt and Adloff, who found an increasing tendency toward the stabilization of defect charge states with increasing degree of hydration in $CoSO_4 \cdot nH_2O$. They agree with Mullen and Ok[12] on the absence of Fe^{3+} in hydrated $CoCl_2$. Ingalls and De Pasquali,[8] on the other hand, show that Fe^{3+} is resolved even in this compound at low temperature, while their room temperature data agree with those of the other two groups. The results suggest either that the stabilization of Fe^{3+} in hydrated salts depends on temperature or that the Fe^{3+} has a much lower effective Debye temperature than Fe^{2+}.

The notion that the Fe^{3+} has a temperature-dependent decay time has been ruled out by delayed coincidence Mössbauer effect experiments in which the spectrum was examined as a function of time during the decay of the excited state[7,13] (Figure 2). These experiments gave no indication of any charge relaxation during the accessible time, *i.e.*, from 0.2τ to 1.7τ, in compounds containing ^{57}Co which show more than one valence state (*e.g.*, $CoSO_4 \cdot 7H_2O$ and $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$). There can be no question but that the ^{57}Co was in the divalent state prior to decay. The most likely conclusion is that charge relaxation goes to completion in a short time compared to the nuclear lifetime, but that there are a number of different final states corresponding to changes in the environment of the ion.

Friedt and Adloff[10,11] have suggested that the environmental change responsible for the stabilization of higher charge states in hydrated compounds is due to the radiolysis of water. This has recently been followed up by Gütlich, *et al.*,[14] and Wertheim and Buchanan.[15] The latter show that ^{60}Co γ irradiation or high-energy electron bombardment of ferrous ammonium sulfate hexahydrate produces a material whose Mössbauer absorption spectrum is similar to the emission spectrum of the ^{57}Co-doped compound (Figure 3). It was also shown that the Auger electron ionization in the molecule containing the ^{57}Co atom was sufficient to radiolyze a water molecule in about one-third of the decay events, a result in good agreement with the experimental yield of Fe^{3+}. The oxidation of Fe^{2+} is thought to be due to the OH radical produced by radiolysis. Electron bombardment of anhydrous salts of Fe^{2+} did not produce any valence change. This mechanism also explains the Fe^{3+} reported by Berger, *et al.*,[16] in a ME experiment using neturon capture by ^{56}Fe to produce the isomeric state of ^{57}Fe in $FeSO_4 \cdot 7H_2O$.

Similar experiments have also been done in various oxalate systems. Sano and Hashimoto[17] report that the decay of ^{57}Co in cobalt(II) oxalate produces only iron(II) oxalate. More recently, Friedt and Asch[18] have shown, however, that small amounts of Fe^{3+} are

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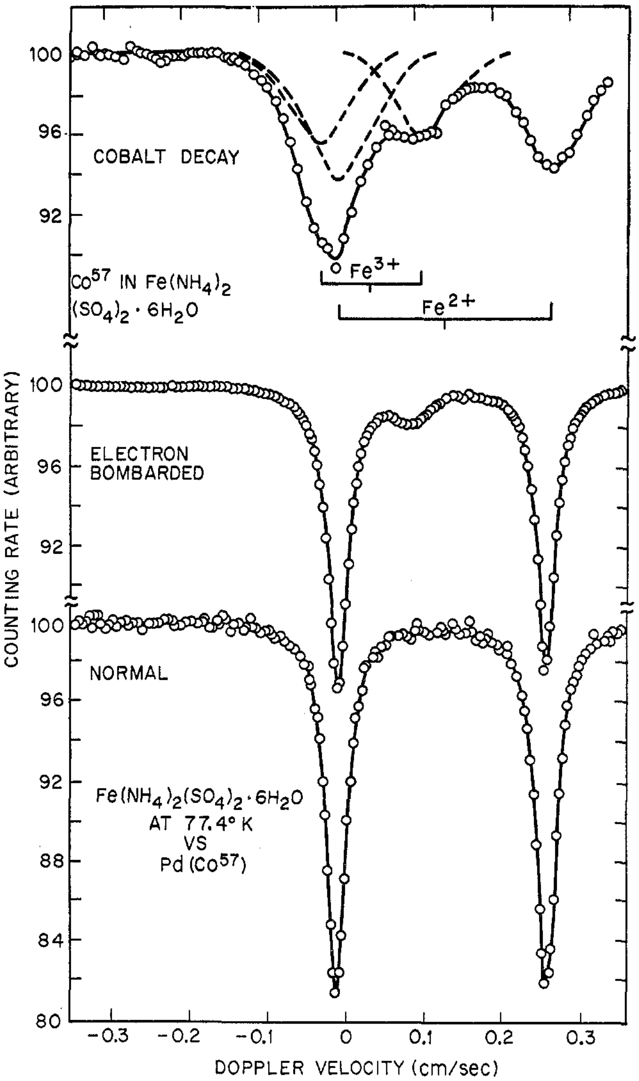

Figure 3. Comparison of radiolysis in $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ with aftereffects in the cobalt-doped compound.

produced in both hydrated and anhydrous cobalt oxalate. In $K_3Co^{III}(C_2O_4)_2 \cdot 3.5H_2O$ the iron was found largely in the divalent state. Sano and Kanno[19] have also reported the reduction of Sn(IV) to Sn(II) in $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ sources containing ^{119m}Sn. In this case Auger electrons result from the internal conversion decay of the ^{119m}Sn.

These results, which at first sight appear contrary to the work on hydrated salts discussed above, are in line with the known reduction of oxalates by radiolysis. The reduction is due to disruption of the carboxyl group with the liberation of CO_2.

Radiolysis by an external source of radiation has also been studied by Mössbauer effect in oxalate compounds. Saito, *et al.*,[20] demonstrated the radiolysis of ferric oxalate ($Fe_2(C_2O_4)_3 \cdot xH_2O$) by ^{60}Co γ rays. About one-half of their material was converted to the ferrous state ($FeC_2O_4 \cdot xH_2O$) by a dose of 200 Mrads. The radiolytic decomposition and thermal annealing of $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ as well as of the anhydrous compound have been studied in detail by Dharmawardena and Bancroft[21] and by Temperley and Pumplin.[22] The radiolytic reduction of ferric citrate has also been observed by Mössbauer effect.[23]

Internal Pressure

Results indicative of chemical changes in the environment following electron-capture decay had also been obtained in a number of molecular crystals quite early in the history of the ME. In cobalt(III) acetylacetonate [Co(acac)$_3$] Wertheim, *et al.*,[24] reported both Fe(II) and Fe(III) after the decay of ^{57}Co(III). The compound was synthesized from cobalt chloride containing the radioisotope and had been repeatedly recrystallized. The trivalent iron had a spectrum like that of iron(III) acetylacetonate; the Fe(II) was identified by its isomer shift. The mechanism originally proposed for the production of Fe(II) was based on the modification of the ligand structure by the highly charged ion produced by Auger effect and subsequent charge relaxation by the iron ion and ligand structure to a new equilibrium state. More recently Hazony and Herber[25] have suggested that the production of Fe(II) is due to an "internal pressure" on the Fe(III) ion. This is based on the finding that in solids at high pressure Fe(III) reduces reversibly to Fe(II) (Drickamer, *et al.*[26]). The "internal pressure" is postulated on the basis of the density difference between Co(acac)$_3$ and Fe(acac)$_3$. The similarity of the spectra of absorbers of Fe(acac)$_3$ under pressure to those of sources of ^{57}Co(acac)$_3$ supports this idea, but does not prove it.

More recently Friedt, *et al.*,[27] have shown that the Mössbauer absorption spectra of electron-bombarded Fe(acac)$_3$ are very similar to the emission spectra after electron capture in ^{57}Co-labeled Co(acac)$_3$. This is a very strong indication that an autoradiolysis mechanism is responsible for the production of the Fe(II); *i.e.*, the mechanism here is similar to that in hydrated salts and oxalates.

Size Effect

The relevance of ionic size to the chemical state of an impurity atom was pointed out by Pollak[5] some years earlier. His analysis suggests that Fe^{3+} should appear in divalent lattices whose metal ion is smaller than Fe^{2+}; *i.e.*, the sense of the effect goes in the opposite direction from that in Co(acac)$_3$. Experimental evidence in support of this suggestion can be found in data on the rutile structure fluorides, MF_2. Only Fe^{2+} was reported following the decay of Co^{2+} in ZnF_2[6] and MnF_2,[28] but in CoF_2 both Fe^{2+} and Fe^{3+} were found.[10,11,29,30]

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Table I

Fractions of Fe^{3+} Produced at Room Temperature by Electron Capture Decay of $^{57}Co^{2+}$ in Various Rutile Structure Fluorides[a]

Compd	Unit cell volume, Å^3	Remarks
MnF_2	78.61	No Fe^{3+} observed
FeF_2	72.99	No Fe^{3+} observed
CoF_2	70.09	~32% Fe^{3+}
ZnF_2	69.32	1% Fe^{3+}
NiF_2	66.69	59%
MgF_2	65.13	82%

[a] The recoil-free fraction is assumed to be the same for Fe^{2+} and Fe^{3+}.

The results of a systematic investigation of the stabilization of Fe^{3+} in rutile structure fluorides by Wertheim, *et al.*,[31] are shown in Table I. There is a strong indication that the smaller Fe^{3+} ion is preferentially stabilized in a lattice site smaller than that of Fe^{2+} in FeF_2.

These results do not imply that differences in ionic size alone are sufficient to account for the stabilization of a defect charge state. Wertheim, *et al.*,[31] assume that a charge-compensating defect, such as a trapped electron, is also required. Cavanagh[29] attributes the effect to a local distortion of the crystal structure produced by Coulomb forces associated with the short-lived high charge states. The nature of this distortion was not further elucidated. Friedt and Adloff[30] assume that charge compensation is provided by ionic vacancies produced by K-capture aftereffects. In particular, they propose a Co^{2+} and a F^- vacancy to maintain charge neutrality near an Fe^{3+} ion. This suggestion also provides a mechanism for the decreasing fraction of Fe^{3+} at high temperature[11] in terms of the thermal annealing (or outward diffusion) of these vacancies. It might be noted, however, that a decrease in the fraction of the higher charge state with increasing temperature is not a common feature of experiments of this type (see ref 11 as well as the discussion of oxides, below).

Similar studies have also been carried out on $CoCl_2$,[29,32,33] $KCoF_3$,[34,35] K_3CoF_6,[35] and $Co(NH_3)_6Cl_2$.[36] An interesting thermodynamic explanation for the stabilization of anomalous charge states of ^{57}Fe after ^{57}Co electron capture has been given by Friedt.[37] She considers the effects of the Madelung potential of the lattice and the ionization potential of the impurity and postulates an excitation energy stored in the lattice near the defect. The results provide an explanation for the size effect in the rutile fluorides.

Coulomb Fragmentation

Recently another mechanism has been advanced in connection with experiments on aftereffects in cobalt chelates. In some cases the data obtained could be explained in terms of radiolytic effects; in others they could not. For example, Nath, *et al.*[38-40] report reduction to Fe^{2+} in one-fourth of the events following the decay of ^{57}Co in tris(dipyridyl)cobalt(III) perchlorate; in bis(indenyl)cobalt(III) perchlorate, however, the emission spectrum was found to bear no resemblance to that of the corresponding Fe(II) or Fe(III) complexes. This was taken as an indication that the original molecule has been destroyed. The mechanism for this process is based on the electrostatic repulsion resulting from the withdrawal of electrons from the ligands by the charge relaxation following the Auger cascade.[41] That is to say, the high positive charge on the metal ion at the end of the Auger cascade is transferred to the ligands. There the missing electrons weaken the bonding, and the net positive charge may be sufficient to destroy the molecule by Coulomb forces. Evidence for molecular fragmentation has also been obtained in tris(phenanthroline)cobalt(III) perchlorate by Jagannathan and Mathur.[42] They further suggest that even the data on tris(dipyridyl)cobalt perchlorate can be interpreted as showing evidence of such fragmentation, but occurring in only a fraction of the events.

Some well-founded skepticism has been expressed[27] regarding the occurrence of this effect in solids where electrons are so readily available to neutralize the high charge state of the Auger core. Radiolysis experiments would be helpful in deciding between these alternatives, but it must be borne in mind that electron bombardment will also knock out K-shell electrons and therefore produce Auger cascades. Ionization effects should, however, be dominant.

Charge Compensation

A great deal of experimental work on the decay products of Co^{2+} has also been done in the NaCl structure oxides. The transition-metal members of this series are well-known defect solids[43,44] whose equilibrium composition is a function of both temperature and oxygen partial pressure. From a microscopic point of view, it is believed that deviations from stoichiometry are realized through the introduction of cation vacan-

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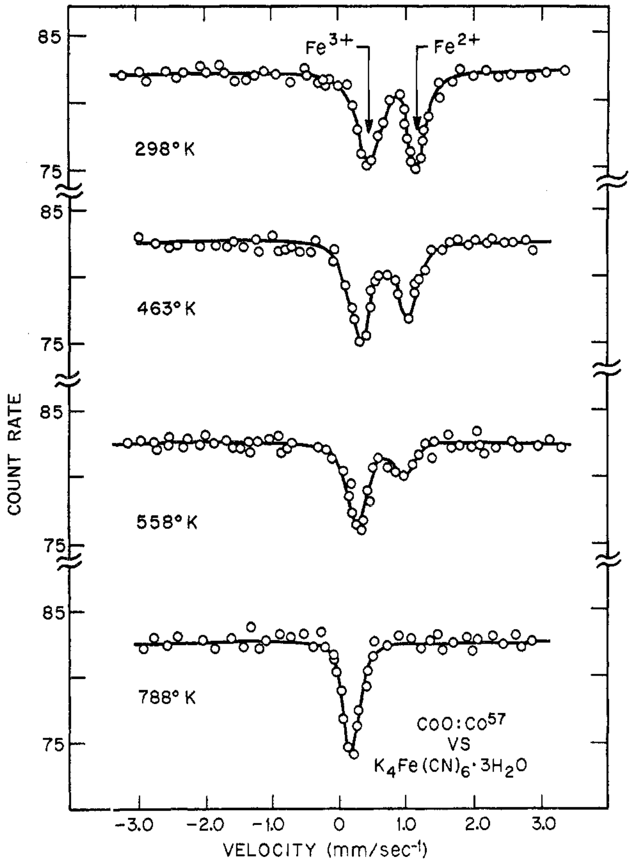

Figure 4. Temperature dependence of valence ratio in CoO (^{57}Co). The Fe^{2+} line vanishes near 788°K (after ref 51).

cies.[45] It is not surprising then that the amount of Fe^{3+} depends critically on sample preparation. It has, in fact, been established that both NiO and CoO can be prepared in which only Fe^{2+} is produced by the decay of ^{57}Co^{2+}.[46-48] The materials which exhibit only Fe^{2+} presumably correspond to oxides closest to stoichiometry, pointing toward the importance of preexisting charge compensating defects.

Of more interest is the behavior of nonstoichiometric material which exhibits both di- and trivalent iron. In CoO and NiO as well as in MnO the fraction of trivalent iron *increases* with temperature in a reversible way and greatly exceeds the fraction of excess oxygen. In CoO this is a clear indication that the trivalent iron is not due to earlier selective oxidation of the ^{57}Co. In NiO all the iron is trivalent above 475°K[49,50] (Figure 4). In CoO the Fe^{2+} is hardly detectable above 800°K.[7,51] In MnO Fe^{3+} was detected at room temperature but not below the Néel temperature of 117°K.[47]

Various mechanisms for the appearance of trivalent iron following the electron-capture decay of ^{57}Co^{2+} in CoO have been proposed. The initial suggestion[52] that the Fe^{3+} may be metastable was subsequently shown to be untenable by delayed-coincidence Mössbauer experiments.[7,13] Another explanation is based on the existence of two types of CoO in which the decay product iron is respectively entirely divalent and entirely trivalent.[48] The first type corresponds to well-known stoichiometric CoO and the second to a composition containing 50% vacancies (later corrected to 25%). The presence of both valences in a single sample was ascribed to the coexistence of both forms in each individual particle of the material. This description closely approaches the normal picture of a defect solid with clustered defects. The nature of the low-density form of CoO has aroused a great deal of controversy.[53,54] It is currently described as a spongelike structure of sintered microcrystals.[55] In this model the temperature dependence of the trivalent fraction depends on the dispersion of the clustered vacancies at high temperature. In a critical experiment Trousdale and Craig[56] have shown, however, that the change in trivalent fraction follows a change in temperature without a measurable time delay and therefore does not allow such diffusive motion to take place.

A third suggestion is that charge relaxation stops at Fe^{3+} in the vicinity of a cation vacancy.[13] The temperature dependence was tentatively attributed to the enhanced diffusive motion of the vacancies at high temperature which favors association with the newly created chemical defects. Localized lattice heating by the preceding decay could also contribute to this effect.

Most recently Leon and Negrete[57] have shown, using a molecular orbital description, that cobalt vacancies should stabilize Fe^{3+} ions in CoO. Their model explains the observed broadening of the Fe^{3+} lines in terms of a superposition of a number of possible defect configurations. They also suggest that the highly charged Auger core would attract cation vacancies from the immediate environment. Following Friedt[20] one might further propose that the highly charged Auger core could actually serve to generate positive ion vacancies by Coulomb repulsion.

In view of the large effort which has gone into the study of CoO it is surprising to find no experiments on material prepared to have a definite composition according to the phase diagram. At present the most satisfactory explanation for the stabilization of defect charge states invokes the presence or production of lattice vacancies in the immediate vicinity of the ion. It is a matter of conjecture whether these vacancies are created in a perfect crystal or whether existing vacancies are made to move in the electric field of the Auger core.

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The finding of large quadrupole splitting and line broadening has been taken as evidence to support this vacancy model. A detailed interpretation of the temperature dependence of the fractions of Fe^{3+} in the light of this model is needed to help put it on a firm footing.

Summary

Changes in the chemical state of ions in solids following nuclear decay processes have been observed by the Mössbauer effect. The mechanisms responsible for these changes are only now being elucidated. In general some modification of the ligand environment appears to be required. These are most often brought about by the radiolytic effects of ionizing radiation. It also appears possible that vacancies, initially present or produced by the Coulomb repulsion of the Auger core, can stabilize new charge states. Other mechanisms which have been invoked are internal pressure effects and the Coulombic fragmentation of molecules by the withdrawal of electrons from the ligands by the Auger core, but there are valid objections to both suggestions. The existence of time-dependent charge relaxation effects has been suggested, but has not been verified experimentally.

Glutamate Dehydrogenase: Anatomy of a Regulatory Enzyme

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In these days of sophistication of scientific research (and I am inclined to use "sophisticated" not only in its modern sense but also in its original connotation), one sometimes encounters doubts as to whether the study of solutions of macromolecules by classical physicochemical means is a meaningful pursuit. We have been caught up in the steamroller of technology. Achievements which provided, a scant two decades ago, in the brilliant minds and hands of the Debyes, the Kirkwoods, the Svedbergs, the Florys, and the Zimms, the tools for a penetrating insight into the world of synthetic and natural polymers have lost much of their glitter for the present day computer-conscious generation of young epigones.

This is not the place to discuss either the considerable achievements in X-ray crystallography or the other, newer, physical techniques (for instance, the unraveling of a large number of protein crystal structures, based on the pioneering and continuing studies of the Paulings, the Kendrews, and the Perutzes) or the deeper philosophical implications of the dehumanizing effect of the computer on science and the human mind. One could call this the "sorcerer's apprentice" effect, in that extrapolation does not necessarily lead to the rewards originally envisaged.

Here I should like to point out that there are fascinating problems related to biomacromolecules, which are clearly important but imperfectly understood, either because they are not yet ripe enough to be dissected by X-rays, nmr, and the newer tools of molecular torture, or because of plain overcrowding in the chambers of inquisition. I should like to show in this Account that, properly coaxed, nature may reveal some of its lesser secrets in the simple, old-fashioned ways. I should like to show that by classical light scattering, sedimentation, viscosity, and related studies we can unravel some of the intricacies of structure and the relation of structure to function of a complex regulatory enzyme, bovine glutamate dehydrogenase.

This is a good place to acknowledge my deep indebtedness to Gordon Tomkins, who in 1966, during my stay at the National Institutes of Health, introduced me to the puzzling aspects of this problem and infected me with the bug of curiosity which has become a steady companion ever since.

The Enzyme: Statement of the Problem

As in all well-organized production schedules, biochemical intermediates in the living cell must be synthesized in closely regulated proportions and suitably linked to the production of related building blocks. The latter are required either for the synthesis of vital macromolecules, in energy cycles, or in processes directed toward storage and utilization of genetic information. In complex biochemical metabolic cycles glutamate dehydrogenase links the carbohydrate Krebs cycle with the pathways of amino acid synthesis. Specifically, it catalyzes the interconversion of glutamic and α-ketoglutaric acids; it performs this function in the mitochondria of the liver. In common with some of the other dehydrogenase enzymes it requires 1 mole of NAD (nicotinamide–adenine dinucleotide) for the reversible stereospecific transfer of 1 mole of hydrogen from its substrate glutamic acid *via* the imino derivative.

This reaction is subject to allosteric regulation and was quoted by Monod, *et al.*,[1] on the basis of the work of Tomkins, *et al.*,[2] in the original exposition of the allosteric hypothesis. A more recent review of allosteric

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