

The Role of Emission Mössbauer Spectroscopy in the Study of Sophisticated Materials*

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Emission Mössbauer spectroscopy is about three orders of magnitude more sensitive than the conventional absorption mode, thereby allowing parts per million substitution of ^{57}Co at the Cu or Mn active site without perturbing the finely-tuned material. ^{57}Co faithfully probes the behavior of Cu-based high temperature superconductors and mixed valence magnetoresistive manganites. The application of emission Mössbauer spectroscopy to biological systems is also highlighted.

1. Electronic Relaxation Following an Auger Event: Whither Goes the Colossal Excitation Energy

A ^{57}Co nucleus undergoes radioactive decay by capturing an orbital electron – most frequently from the K-shell. It triggers Auger ionization and thus the vacancy cascades traverse to the valence shell, resulting in a multiply-charged ionic species. Pollak¹ estimated that the maximum charge build up for the daughter ^{57}Fe as +8, viz Fe^{8+} . The Auger vacancy cascade occurs in about 10^{-16} s. This charge is rapidly neutralized by transfer of electrons from neighboring atoms in the molecule. This redistribution of charges in the molecule would occur within 10^{-15} s, and therefore without any change in the relative positions of the individual constituent nuclei. In the gas phase, several researchers have shown that the multi-center Coulombic repulsion explodes the molecule containing $^{80\text{m}}\text{Br}$, leading to formation of several highly charged fragments.^{2,3} A similar picture of disruption of molecules in liquids has been observed by Libby,⁴ among others. We initiated Mössbauer investigations on a variety of cobalt complexes incorporating ^{57}Co during 1966/1967 while I was visiting the Nobelist Libby's laboratory at UCLA and then continued these studies while visiting Nobelist Calvin's laboratory in UC Berkeley. Libby, who was conditioned by the Auger after-effects in gas and liquid phase, was not particularly thrilled by our venture. He commented, "What can you learn about a crystal vase using a sledge hammer?" His concern was that all cobalt complexes would succumb to the Auger event.

However, in a solid, things could be different. We found that most of the cobalt complexes fragment and show spectra of $\text{Fe}^{2+}/\text{Fe}^{3+}$. On the other hand, complex molecules with conjugated ring systems (having delocalized electrons), such as cobalt phthalocyanine, tris-bipyridyl Co(III) perchlorate, and vitamin B₁₂, escape fragmentation in 100% of the Auger events.⁵⁻⁷ As a spin-off, we could follow directly the electronically-excited isotopic exchange of carrier-free $^{57}\text{Co}^{++}$ with complexed Co in $\text{Co(III)(bipy)}_3(\text{ClO}_4)_3$ using emission Mössbauer spectroscopy (EMS).⁸ We also found that the probability of fragmentation depends on the degree of conjugation in the molecule.⁹ It was not surprising that molecules of several cobalt complexes fragment following the Auger event, as predicted by Libby. What was amazing was that some molecules which have conjugated ligands with delocalized π -electrons escape fragmentation. We proposed the following model: There is a large charge built up on the molecule following the Auger

event. It is followed by electronic relaxation, with electrons flowing from neighboring molecules depositing tens of eV electronic excitation energy. The molecule has to get rid of this energy in less than 10^{-14} s to escape fragmentation. Energy dissipation through radiationless transitions is a slow process. We proposed that the delocalized π -electrons undergo collective excitation and that the plasmon decays in $<10^{-14}$ s, transferring practically all of its energy to a single electron, which is emitted.^{9,10}

The proposed novel mode of dispersal of colossal electronic excitation (>50 eV) from a molecule remained unnoticed due to benign neglect or skepticism until recent photoemission studies of C₆₀ and C₇₀.^{11,12} The European scientists illuminated fullerenes with photon energies of 5 to 50 eV and observed that the photo-ion yield is dominated by a strong resonance at about 20 eV. The results were interpreted invoking collective excitation of π -electrons either by a single or a high intensity multi-photon process. The plasmon is strongly coupled to single electron continuum states, and the plasmon decay is associated with an ejection of an electron, which overshadows the direct photo-ionization process. Our prior work was not cited. We submit that the strong coupling is not confined to C₆₀ and C₇₀ molecules as alluded to by the authors, but that all molecules with a large number of delocalized electrons would exhibit this novel mode of self-protection.¹³ Why the plasmons are not coupled to single electron continuum states in covalent compounds with no conjugation (and thereby offer no self-protection from fragmentation) is not known and remains a fertile area for investigation by theorists.

2. What Is the Spin-Off Arising from These Emission Mössbauer Studies?

First, EMS can be very valuable in the study of biological processes, especially for systems having a fair degree of conjugation, e.g., vitamin B₁₂, hemoglobin and zinc fingers. EMS is about three orders of magnitude more sensitive than the conventional absorption mode. ^{57}Co has a theoretical specific activity of 310 GBq/mg, and so a couple of micrograms of ^{57}Co will suffice for measurements. Secondly, one can substitute minuscule amounts of ^{57}Co for Cu in high temperature superconductors and for Mn in mixed valence magnetoresistive manganites without perturbing the systems. Both systems have delocalized electrons for plasmon formation followed by de-excitation with transfer of energy to an emitted electron, and thereby escaping damage arising from Auger after-effects. It may be noted that for purely ionic systems with little covalence, presence of delocalized electrons is not a prerequisite for EMS

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investigations.

To give readers a flavor as to how EMS can be used to study biomolecules and to probe microscopic behavior in materials, I will mention a few highlights of our findings.

3. Emission Mössbauer Studies of Cobalamins

Large conformational changes in the porphyrin ring, as exhibited by isomer shift and quadrupole splitting, were observed just by hydrolysis of a couple of propionamide side chains. We suspect that conformational isomerization precedes hydrolysis. Simple hydrolysis of a couple of side chains far removed from ^{57}Co sitting in the center of the porphyrin ring should not bring about such drastic changes in Mössbauer parameters.¹⁴ Modern fast techniques in NMR spectroscopy can hopefully detect a short-lived conformational isomer preceding hydrolysis of Vitamin B₁₂.

4. Emission Mössbauer Study of Cooperativity in Hemoglobin

Cobalt substitution for Fe in the porphyrin ring does not bring about any major change in the general function of hemoglobin (Hb), namely to pick up oxygen in the lungs and to transport it to the muscle tissues with high efficiency. Once a sub-unit of Hb picks up oxygen, it transmits the message to the remaining three sub-units to do the same with higher affinity, and then unloads the cargo with high efficiency where ever required. This cooperative behavior has been a challenging problem for biochemists and continues to be so even at present. Research in the area of cooperativity of Hb was completely dominated by Perutz's model for several years. An important feature of Perutz's trigger mechanism for cooperativity in the reversible oxygenation of Hb was the tension along the histidine-metal linkage in deoxy Hb and deoxy cobalt Hb (CoHb), supposedly due to the pull exerted by the globin on the metal atom. We attempted to verify the existence of this pull by studying the emission Mössbauer spectra of deoxy- $^{57}\text{CoHb}$, oxy- $^{57}\text{CoHb}$, oxy- $^{57}\text{CoMb}$ and $^{57}\text{Comet-Hb}$. For none of these CoHb and myoglobin, the emission Mössbauer spectrum matched with the absorption spectrum of the corresponding iron analog. These observations indicate that the daughter ^{57}Fe atom is "frozen" almost in the same spatial situation as that of the parent ^{57}Co . *The protein is apparently holding the cobalt atom in position rather rigidly and after the electron capture decay of the ^{57}Co atom, the protein does not permit the daughter ^{57}Fe to move to a position characteristic of the iron atom in the time scale of Mössbauer emission.*¹⁵ Our EMS investigations show the absence of tension in the Co/Fe bond as proposed by Perutz. However, this area of research is still important especially due to the finding that there are several intermediate states between the completely fully oxygenated "relaxed" state and the "tense" deoxygenated one. EMS can also provide valuable information about the conformational changes occurring in sickle-cell anemia.

5. Emission Mössbauer Studies of Some Outstanding Problems in High Temperature Superconductivity

Mössbauer spectroscopy provides a very valuable tool for obtaining information on the nanoscopic level of a local site. *Emission Mössbauer spectroscopy is much more sensitive than the regular absorption mode. For emission Mössbauer effect studies, a few tens of parts-per-million of Cu are substituted by ^{57}Co with minimal perturbation of the system.* ^{57}Co faithfully microprobes subtle changes in the electron density, local dynamics, presence of extraneous oxygen and magnetic behavior. A few examples of our studies, which led to a better understanding of some superconducting systems, are mentioned below.

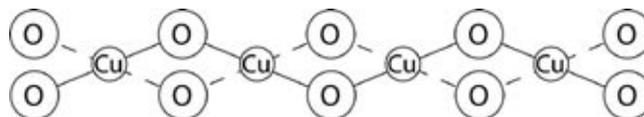


Figure 1. Diffraction studies could not decide positional disorder of O^{2-} .

A high resolution neutron powder diffraction study showed that the Cu-O chain in $\text{YBa}_2\text{Cu}_3\text{O}_7$ is zigzag with two potential minima for the O^{2-} ions at about 0.015 nm on either side of the chain. Neutron diffraction could not tell whether the zig-zag configuration is static or dynamic with O^{2-} oscillating between the split-sites. It has been proposed earlier that should the oxygen ions be moving in a double-well potential that would result in an extraordinary enhancement of the electron-lattice coupling which would explain the high superconducting transition temperature. Our Mössbauer studies show that the oxygen ions are not stationary but oscillate between the two potential wells.^{16,17} We also find that partial substitution of yttrium by praseodymium in the system results in dampening and finally killing of this oscillation. This correlates well with the deleterious effect of Pr on superconductivity.^{16,17}

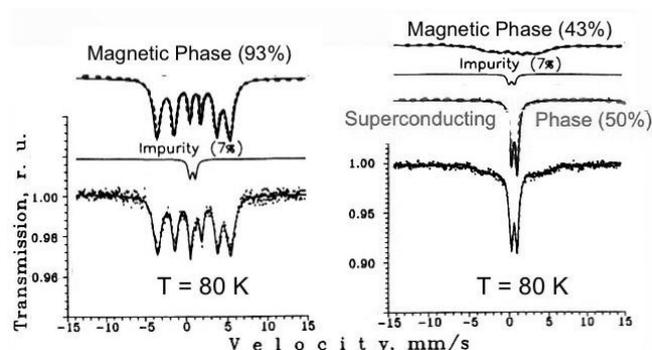


Figure 2. Mössbauer spectra of as prepared and deoxygenated $\text{Nd}_{2-x}\text{Ce}_x\text{Cu}(\text{}^{57}\text{Co})\text{O}_4$.

The electron-doped material $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ becomes superconducting with a Ce^{4+} content around 0.16, but only after removal of a minuscule amount of extraneous oxygen. This enigmatic behavior has attracted considerable attention. We find that the presence of a minuscule amount of oxygen results in the localization of the static magnetic order in the Cu-O plane. These microscopic spin clusters have variable size centered around 10 nm. Upon slight deoxygenation, a major fraction of spin clusters associated with a six line spectrum vanishes, and converts to a paramagnetically relaxed species with a doublet, which is the signature of the superconducting phase. The Mössbauer parameters also indicate that Nd-Ce-Cu-O is a truly electron-doped superconductor contrary to several reports in the literature.¹⁶⁻¹⁹

The Mössbauer studies of $\text{HoNi}(\text{}^{57}\text{Co})\text{B}_2\text{C}$ provide a direct evidence for the electronic phase inhomogeneity in the material.²⁰

6. Emission Mössbauer Studies of Magnetoresistive Manganites

On substitution of Ca^{2+} for La^{3+} in LaMnO_3 , the compound $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ becomes a ferromagnetic metal for $0.18 \leq x < 0.5$. The hopping of an electron from Mn^{3+} to O^{2-} is associated with a simultaneous hop from the latter to Mn^{4+} . The probability of the hopping by this double exchange (DE) is the highest when both hopping electrons have the same spin orientation requiring Mn ions to be ordered ferromagnetically. The metal-

lic behavior is synergistically associated with the ferromagnetic order through electron hopping. The resistivity increases considerably near the Curie temperature (T_C). On application of a magnetic field near T_C , there is a dramatic decrease in resistivity due to regeneration of metallicity. The origin of this colossal magnetoresistivity (CMR) is rather enigmatic and has attracted lot of attention from researchers. In short, what was baffling the scientific community was as to how a moderate magnetic field could convert what was believed to be a paramagnetic state to a ferromagnetic one. We have addressed this problem using emission Mössbauer spectroscopy where the local probe $^{57}\text{Co}/^{57}\text{Fe}$ substituting minuscule amount of Mn atoms senses the microscopic behavior of the material. Only a few parts per million substitution of Mn atoms with ^{57}Co substituting minuscule amount of Mn atoms senses the microscopic behavior of the material. We find that, surprisingly the long range ferromagnetic order starts breaking down below the Curie temperature (T_C) and the material degenerates into nano-size spin clusters which fluctuate rapidly and exhibit superparamagnetic-like behavior. On a time scale of 10^{-8} s, the spin clusters exhibit minimal lattice distortions. These spin clusters survive well above T_C , and would very effectively increase bulk resistivity due to their rapid fluctuations. On application of an external magnetic field, the small magnetic clusters coalesce to form larger ones with more ordered spins, and the material shows enhanced conductivity through percolation. This provides a rationale for observation of magnetoresistivity in manganites.²¹⁻²⁴ EMS investigations permit us to conclude that, the break up into small rapidly fluctuating spin clusters near T_C and thereby exhibiting superparamagnetic-like behavior is a prerequisite for observing bulk colossal magnetoresistivity.

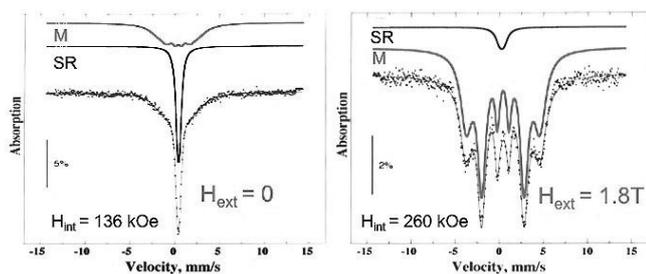


Figure 3. Mössbauer spectra of single crystal $\text{La}_{0.9}\text{Ca}_{0.1}\text{Mn}(^{57}\text{Co})\text{O}_3$ at $T=175\text{K}$.

7. Conclusions

We find that complex molecules with conjugated systems having delocalized electrons escape fragmentation following the Auger event. The huge amount of electronic excitation energy deposited during neutralization of the built-up charge results in collective excitation and formation of plasmon. The plasmon decays transferring all its energy to an electron, which leaves the molecule unscathed. This opens up the possibility of using emission Mössbauer spectroscopy to systems with delocalized electrons like superconductors, and mixed valence magnetoresistive manganites and some biological systems.

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