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IRON AFTER  $^{57}\text{Co}$  ELECTRON CAPTURE IN Co COMPLEXES

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ON THE MECHANISM OF FORMATION OF ANOMALOUS CHARGE STATES OF  
IRON AFTER  $^{57}\text{Co}$  ELECTRON CAPTURE IN Co COMPLEXES

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ABSTRACT

The Mössbauer absorption spectra of ferric acetylacetonate irradiated with electrons are found to be similar to the emission spectra after EC in  $^{57}\text{Co}$  labeled  $\text{Co}(\text{AcAc})_3$ . This result indicates that an autoradiolysis mechanism is responsible in molecular compounds for the stabilization of the anomalous iron charge states.

The physico-chemical consequences in the solid state of the Auger cascade following nuclear processes have been the object of a number of studies in the last years. Extensive results of Mössbauer emission spectroscopy of  $^{57}\text{Co}$ , embedded in a variety of matrices, have been reported. Whereas there is generally good agreement among independent experiments, the mechanisms of stabilization of the defect charge states remain controversial.

The multiply charge species of  $^{57}\text{Fe}(\text{Fe}^{n+})$ , where  $n \leq 7$  after EC in  $^{57}\text{Co}^{2+}$  are formed in a time of about  $10^{-15}$  sec, during the Auger cascade which follows the orbital electron capture (EC) process. The neutralization is expected to

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proceed rapidly in the solid phase. Mossbauer emission spectroscopy allows the detection of those ionic species whose life time is comparable or higher than the nuclear half life of the first excited state of  $^{57}\text{Fe}$  ( $10^{-7}$  sec). Time delayed coincidence measurements ruled out the hypothesis that charge relaxation proceeds upon such a time scale <sup>1</sup>.

It has been suggested that the ionic size of the iron species should be a determining factor for its stabilization, i.e.  $\text{Fe}^{3+}$  might be stabilized in a lattice which is too small to accommodate the larger  $\text{Fe}^{2+}$  ions <sup>2</sup>. An alternative explanation was based upon the known reduction of ferric ions under pressure: as the ionic radius of  $\text{Fe}^{3+}$  is larger than that of  $\text{Co}^{3+}$ , it was suggested that an internal pressure could manifest itself upon the normally charged ions ( $\text{Fe}^{3+}$ ) and induce the appearance of the reduced species ( $\text{Fe}^{2+}$ ) <sup>3</sup>. Recent experiments have shown that this explanation is insufficient: the emission spectra of potassium trisoxalatoferrate (III) and potassium trisoxalatocobaltate (III), both labelled with  $^{57}\text{Co}$ , are quite similar, although such a pressure effect only applies to the second compound <sup>4</sup>.

We have suggested that the stabilization of the anomalous ionic species of iron formed after  $^{57}\text{Co}$  EC in complex ligand compounds can be understood on the basis of a process of autoradiolysis by the Auger electrons and the X-rays; the autoirradiation creates unstable radicals, whose oxidation-reduction properties will determine the final state of the iron ions <sup>5</sup>. This interpretation has been supported by the analogy observed between the emission spectra in various  $^{57}\text{Co}$  labelled complexes and the absorption spectra of the corresponding compounds of iron after irradiation with an electron beam or an external source of  $\gamma$ -rays <sup>6</sup>.

More recently, another mechanism has been proposed for the case of molecular

crystals, which states that the multiply charged daughter iron ions are rapidly neutralized through the transfer of electrons from the ligands and that the multi-center coulombic repulsion between the charged ends leads to a coulombic explosion of the complexes. There is considerable evidence supporting this mechanism in the case of isolated gaseous molecules. It appears, however, that this mechanism is less probable in the condensed phase. This mechanism has been invoked to interpret the emission spectra of  $^{57}\text{Co}$  labelling a number of molecular cobalt complexes, and in particular of  $\text{Co(III) acetylacetonate}$  <sup>7</sup>. In order to decide between the two interpretations, we studied the effects of the irradiation of ferric acetylacetonate by an electron beam for it can be assumed that the auto-irradiation process is well simulated by a radiolysis experiment using an external source of irradiation.

Ferric acetylacetonate was irradiated with a beam of 2 MeV electrons, at a current of 5  $\mu\text{A}$  during a time period of 15 to 30 minutes. During the irradiation, the target was enclosed in vacuo at a temperature of about 115<sup>o</sup>K. The spectra were obtained with a conventional constant acceleration spectrometer; the absorbers were kept at liquid nitrogen temperature in the same cryostat as that used for the irradiation experiments.

New peaks, which can be assigned to the presence of highspin ferrous ions, appeared in the Mössbauer absorption spectrum after irradiation. The spectral peaks were decomposed into two doublets, one of which characterizes  $\text{Fe(AcAc)}_3$  and the other, with an isomer shift of 1,35 mm/sec against iron metal and a quadrupole splitting of 2.30 mm/sec at 80<sup>o</sup>K is typical of ferrous ions. An increase of the proportion of ferrous ions with the time of irradiation was observed.

An annealing at room temperature of the irradiated compounds induces a progressive reappearance of the spectrum of the original acetylacetonate; after 12 hours

of annealing at 295°K, the spectrum is quite similar to that of the complex before irradiation (Fig. 1).

The most interesting point concerns the comparison of the spectra obtained after irradiation with the emission spectra of the corresponding  $^{57}\text{Co}$  labelled cobalt complex: the shapes of both spectra are similar, and a comparison of the hyperfine interaction parameters leaves little doubt that both processes lead to the same forms of stabilization of the iron ions (Fig. 2).

#### CONCLUSION

This result confirms that the mechanism of formation of anomalous oxidation states of iron after  $^{57}\text{Co}$  EC involves a process of autoradiolysis of the ligands: the electrons, which are emitted during the Auger cascade, have a low energy so that their mean path is short. The autoradiolysis is limited to the nearest neighbours of the decayed nucleus, whose final charge state will be determined by the oxidizing or reducing properties of the radicals which are created by this mechanism.

It is important to observe that all the large conjugated molecules, whose  $^{57}\text{Co}$  complexes were observed by Nath et al. <sup>7</sup> to have no after effects, have strong radioresistant properties. On the other hand, most of the chelates where molecular disruption has been invoked are known to be highly radiosensitive.

FIGURE CAPTIONS

Figure 1: Mössbauer absorption spectra of ferric acetylacetonate at 80°K (source  $^{57}\text{Co/Pd}$ ):

- a) before irradiation
- b) after irradiation with 2 MeV electrons, 5  $\mu\text{A}$  during 15 min.
- c) after 12 hours annealing at room temperature.

Figure 2: Comparison between:

- a) the emission spectrum of  $^{57}\text{Co}(\text{Acac})_3$  at 77°K (from ref. 7) (upper velocity scale) and
- b) absorption spectrum at 80°K of  $\text{Fe}(\text{Acac})_3$  after irradiation (lower velocity scale).

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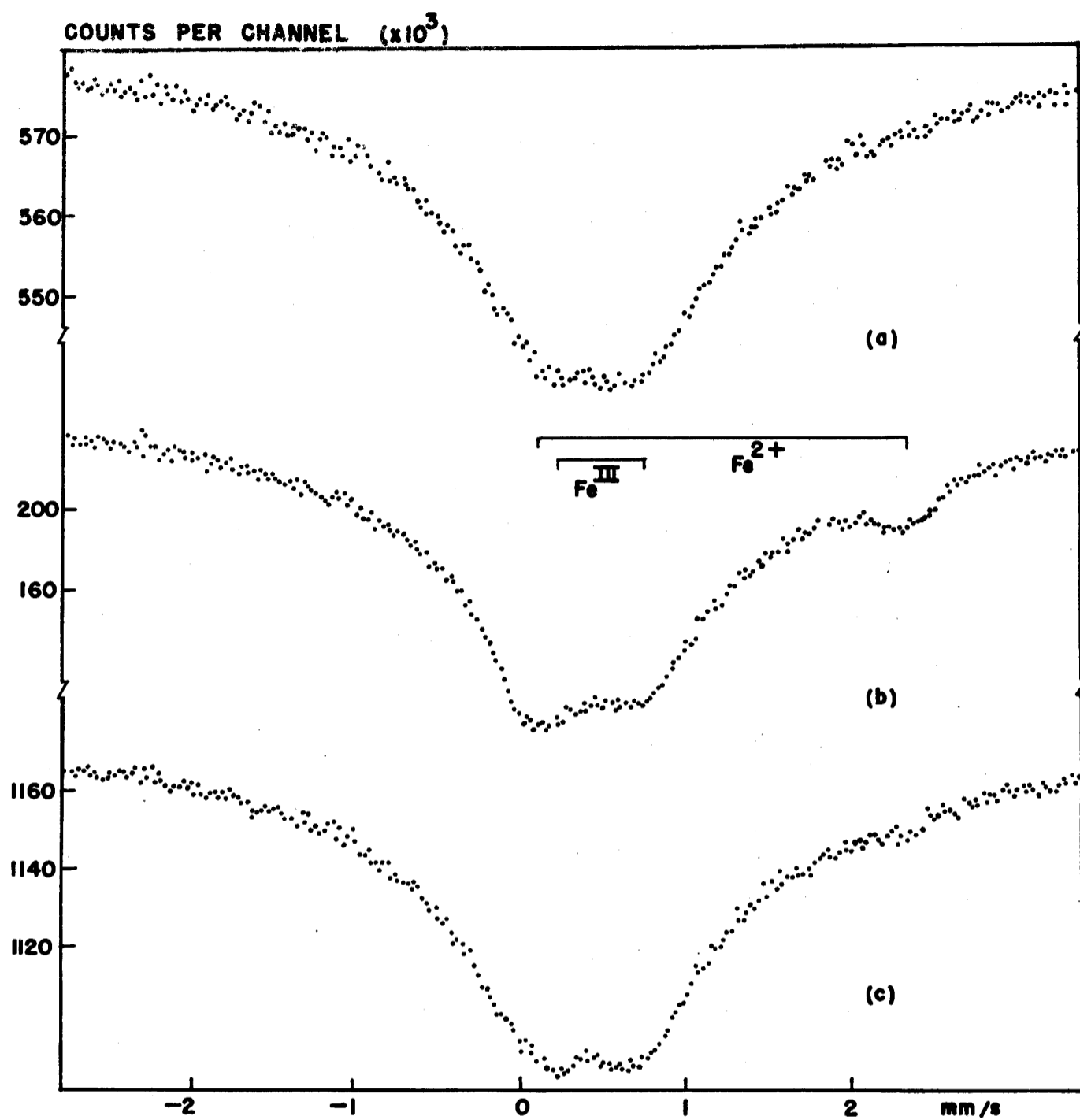


FIG. 1

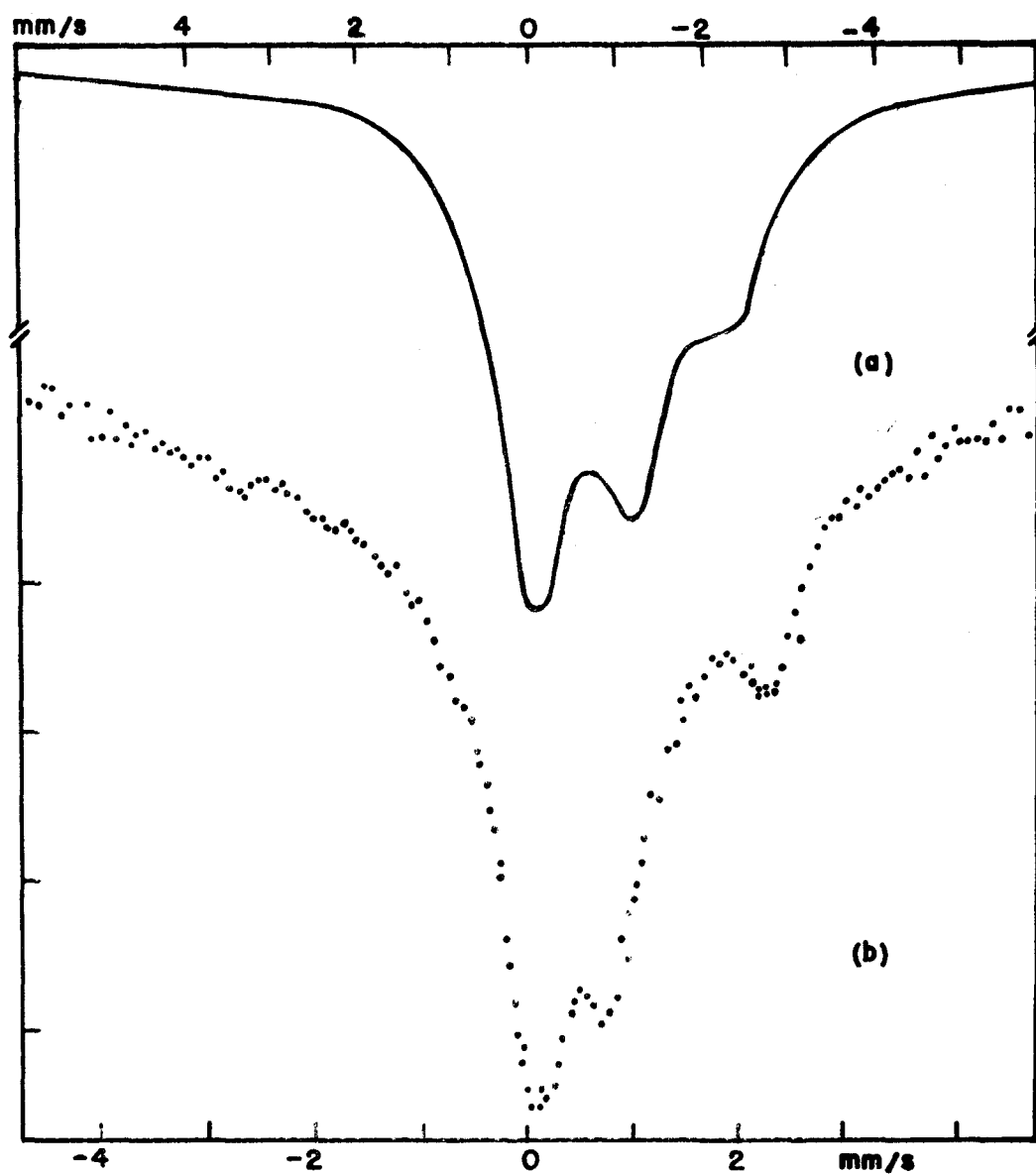


FIG. 2