Hyperfine Interact (2006) 167:881–885
DOI 10.1007/s10751-006-9373-7

Effects of trapped electrons on the line shape in emission Mössbauer spectra

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Published online: 14 November 2006

Abstract To explain line broadening in emission Mössbauer spectra as compared to the corresponding absorber measurements, the model of trapped electrons has been proposed. Auger electrons (emitted, e.g. after electron capture by ^{57}Co or after the converted isomeric transition of ^{119m}Sn), as well as secondary electrons, may be trapped in the proximity to the nucleogenic ion. Electrons captured by lattice traps at different distances from the daughter ion induce an asymmetric distribution of quadrupole splitting in the resulting emission spectra, as shown in a few examples. This model is supported by estimates of quadrupole splitting values which may be caused by such trapped electrons located at specified distances from the nucleogenic atom.

Key words trapped electrons · line broadening · emission Mössbauer spectroscopy · quadrupole splitting distribution function

1 Introduction

Resonant lines in emission Mössbauer spectra can be significantly broadened as compared to those in transmission spectra. Line broadening in emission spectra is observed for many

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isotopes, but more often and with more evidence in experiments with ^{57}Co [1, 2] and ^{119m}Sn [3] in solids. Note that in both the two types of nuclear decay for ^{57}Co and ^{119m}Sn (via electron capture and converted isomeric transition, respectively), an electron vacancy in an internal shell of the daughter atom is formed. Filling in this vacancy results in the emission of X-ray radiation or electrons owing to the Auger effect. For electron emission, while an electron hole moves to the outer levels, the more Auger transitions take place, the higher the degree of ionization of the atom. The emitted electrons induce numerous physical and chemical processes within the environment of the daughter atom [4, 5], leading to the broadening of resonant lines, especially in molecular and non-crystalline compounds.

Line broadening is often ascribed to the states of the nucleogenic atoms featured by various slightly different microenvironments. A possible reason for their appearance was proposed for ^{57}Co in CoO [2] as a consequence of electron capture by Fe^{4+}, formed owing to the Auger ionisation, from a neighbouring Co^{2+}, producing Co^{3+}. Thus, a wide range of local environments could be produced resulting in small differences in the field at the Fe nuclei. However, line broadening was later shown [6] to be caused by the presence of defects in the initial CoO. This mechanism cannot account for line broadening in more complex molecular compounds. Attempts were also made [7] to explain line broadening by the formation of various chemical forms of the nucleogenic ion.

In our earlier work [8], the disappearance of the hyperfine magnetic structure in emission Mössbauer spectra was observed, which was interpreted as a consequence of the formation of trapped electrons participating in spin exchange with the daughter ion. In this work, a deeper analysis of emission Mössbauer spectra has been performed in order to find the evidence for such trapped electrons.

2 Materials and methods

The ^{57}Co-containing systems under study were: sample 1, a dry complex of anthranilic (*o*-aminobenzoic) acid with $^{57}Co^{2+}$ (carrier-free; 3.7×10^7 Bq); sample 2, a dry complex of indole-3-acetic acid with $^{57}Co^{2+}$ (also carrier-free; samples 1 and 2 were obtained by drying 1.0 ml of 1 mCi $^{57}Co^{2+}$-containing aqueous solution of a corresponding acid, taken in a large excess with regard to $^{57}Co^{2+}$, in air); sample 3, a solution of $^{57}CoCl_2$ in ethanol (containing also 4 M carbon tetrachloride) rapidly frozen in liquid nitrogen. The ^{119m}Sn-containing system (sample 4) was represented by ethanolic solutions of $^{119m}SnCl_2$ with different concentrations of $CrCl_2$ (added as an electron scavenger) rapidly frozen in liquid nitrogen. Other details of emission Mössbauer measurements and statistical treatment of the experimental data were described elsewhere [8–11].

3 Results and discussion

Emission (^{57}Co) Mössbauer spectra measured at T=293 K (sample 1) and at the temperature of liquid nitrogen (samples 2 and 3), are presented in Figure 1a–c. Each of the three spectra shows a superposition of two doublets related to $^{57}Fe^{2+}$ and $^{57}Fe^{3+}$ ions forming from the parent $^{57}Co^{2+}$ ions owing to competitive reactions of non- or weakly bound electrons in the medium [9]. The components of the spectra are essentially broadened and are typical for locally non-uniform systems [12, 13]. Processing and analysis of

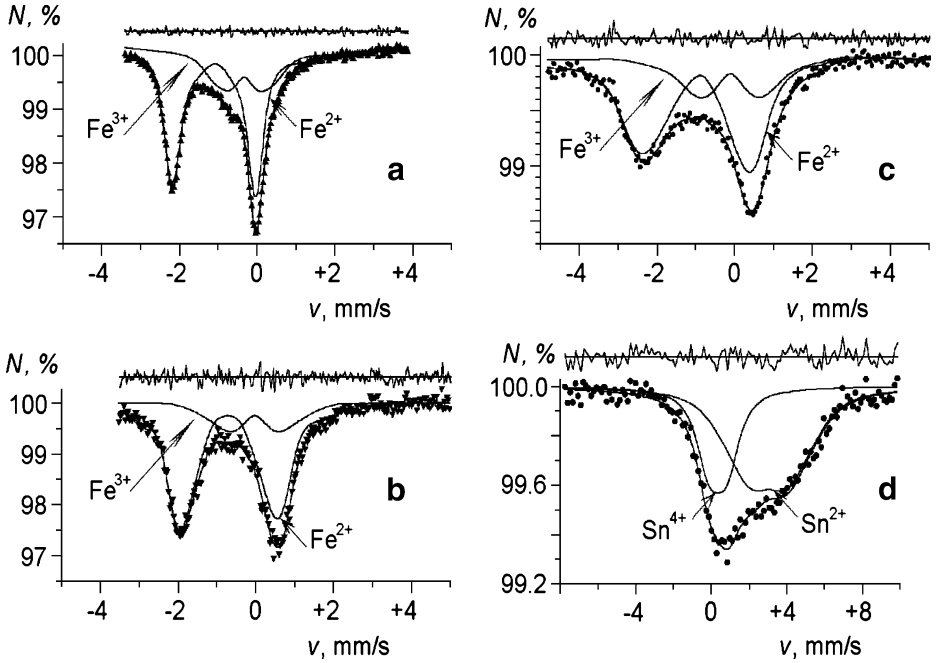

Figure 1 Emission Mössbauer spectra of $^{57}Co^{2+}$-containing complexes of **a** anthranilic acid and **b** indole-3-acetic acid in the dry state, as well as **c** $^{57}CoCl_2$ solution in ethanol with 4 M CCl_4 and **d** $^{119m}SnCl_2$-containing ethanol solution with $CrCl_2$ added as an electron scavenger (see text) rapidly frozen in liquid nitrogen. *N* Transmission (%), *v* velocity (mm/s); measured at T=293 K for **a** and at T=80 K for **b**–**d**.

the spectra were carried out by extracting two independent distribution functions $p(\Delta)$ of quadrupole splitting Δ for excited nuclear levels of the ^{57}Fe nucleus with the spin 3/2 [13] using the program DISTRI from the program complex MSTools [12].

The results of extraction of the distribution functions $p(\Delta)$ corresponding to $^{57}Fe^{2+}$ and $^{57}Fe^{3+}$ ions are presented in Figure 2. All the distribution functions are featured by asymmetric dome-shaped curves with a somewhat less steep slope at larger Δ values, which is more expressed for $^{57}Fe^{3+}$ ions (see the left-side upper plot in Figure 2). Such a shape of the $p(\Delta)$ function can be induced by charged particles located in the vicinity of Fe atoms at various distances from them. Considering the processes of post-decay relaxation of the system, electrons can be the most probable charged particles capable of creating a large electric field gradient.

The above model is supported by estimations of Δ values that could be created by a single electron located at distances 2, 1.5 or 1 Å from Fe ions (see the numbers at the vertical dashed lines in Figure 2). Calculation of the electric field gradient was carried out on the assumption of point localization of charges using the program LATTICE [12]. The quadrupole moment value of a ^{57}Fe nucleus in the excited state, Q=0.146 b [14], and the Sternheimer antishielding factors for Fe^{3+} ($\gamma_\infty = -9.14$) and for Fe^{2+} ($\gamma_\infty = -11.5$) [15] were used. According to these estimations, such a trapped electron can induce alterations in the electric field gradient. Thus, trapped electrons located at different distances from the nucleogenic atom can induce an asymmetric distribution of Δ. As an alternative to such trapped electrons, one may consider the formation of radicals near Fe atoms, or ion-radicals

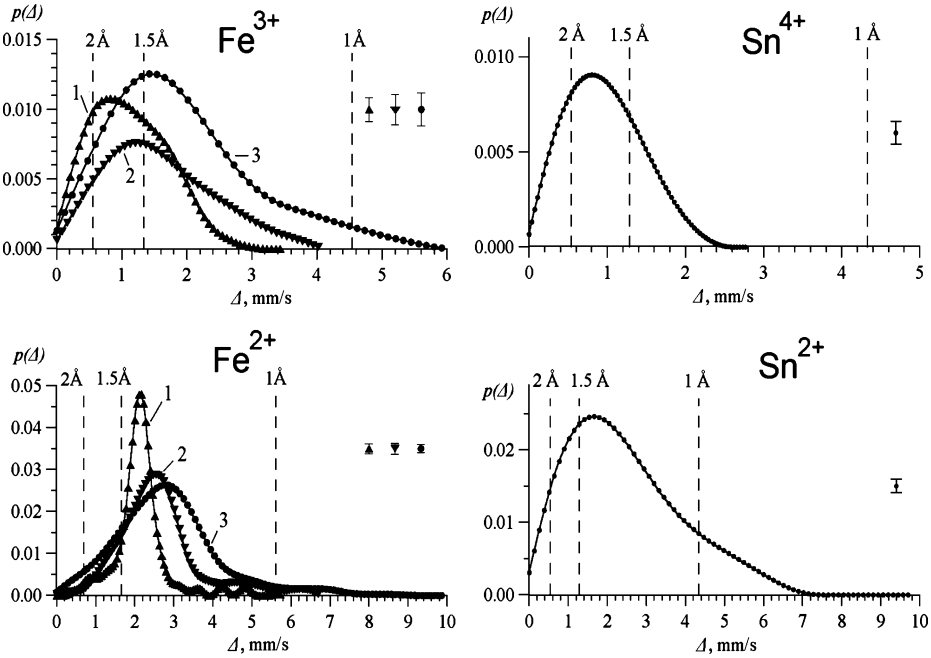

Figure 2 Distribution functions $p(\Delta)$ of quadrupole splitting (Δ) calculated for the components of emission (^{57}Co) Mössbauer spectra a–c presented in Figure 1 (see text) for the nucleogenic $^{57}Fe^{2+}$ (*left-side lower plot*) and $^{57}Fe^{3+}$ (*left-side upper plot*), as well as for the components of emission (^{119m}Sn) Mössbauer spectrum d presented in Figure 1 (see text) for Sn^{2+} (*right-side lower plot*) and Sn^{4+} (*right-side upper plot*). For the *vertical dashed lines*, see text.

more strongly influencing the electric field gradient. However, this seems less probable as, first, such radicals can form not in all systems and, second, electrons therein are valent with more delocalised wave functions and would therefore induce smaller electric field gradients. Note also that in the transmission Mössbauer spectra of the similar complexes containing Fe^{2+} and/or Fe^{3+} ions [16, 17], the line width values can be considered as normal considering the thickness of the samples, and the distribution of quadrupole splittings was symmetric.

A similar asymmetric distribution of Δ was also observed in emission spectra involving the isotope ^{119m}Sn. In Figure 1 (plot d), a spectrum is given of frozen ethanol solution containing $^{119m}SnCl_2$. For improving the statistics, the spectrum was obtained by summing up several spectra of the same type [10] in the presence of different concentrations of $CrCl_2$ which had been added as an electron scavenger. The large line width values observed for both Sn^{2+} and Sn^{4+} are indicative of non-uniformity of the system. In this case, the distributions of Δ are also asymmetric (Figure 2; right-side plots) and less steep at larger Δ values. In Figure 2 (right-side plots), dashed lines also represent the results of calculation of Δ according to the model used in the ^{57}Co emission experiments (see above and Figure 2, left-side plots). The quadrupole moment of the ^{119}Sn nucleus in the excited state, $Q = -0.109$ b [18], and the Sternheimer antishielding factor for Sn^{2+}, $\gamma_\infty = -21$ [15], were taken for calculations (the same value of γ_∞ was used for Sn^{4+} owing to the lack of relevant data in the literature for Sn^{4+}).

4 Conclusions

Line broadening in emission Mössbauer spectra can be caused by the formation of trapped (solvated, hydrated) electrons. Electrons trapped at various distances from the daughter ion induce distortions of the line shape which is described by an asymmetric distribution function for quadrupole splitting. Thus, the line shape may serve as a basis for estimating the distribution of trapped electrons in the vicinity of the daughter ion. Broadening is more strongly expressed for disordered systems which contain many traps for electrons.

Acknowledgements This work was supported in parts by the Russian Foundation for Basic Research (Grant 05-03-33079), NATO (Grants LST.NR.CLG.981092 and CPB.NR.NREV.981748), as well as under the Agreement on Scientific Cooperation between the Russian and Hungarian Academies of Sciences for 2002–2004 and 2005–2007.

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