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Applications of Mössbauer goodness-of-fit parameters to experimental spectra: Further discussion

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As I write this fourth comment on my original paper (Dyar, 1984, was followed by Waychunas, 1986; Dyar, 1986; and Waychunas, 1989), it is apparent that Waychunas and I have fundamentally different (and apparently irreconcilable) perspectives on the important issues in Mössbauer spectroscopy *that have already been clearly expressed.* Therefore, I believe that it is not constructive to argue further over the semantics of what constitutes "random noise" versus "systematic spectal distortion." I also refuse to be drawn into further arguments over the different MISFIT parameters used by the two researchers, beyond commenting that we must henceforth be careful to distinguish between Ruby's (1973) MISFIT (which is the standard in the field) and Waychunas' new term M′ as posed in his original (1986) reply. My purpose in writing this comment is to clarify two new issues raised in the most recent discussion and then let the matter rest.

Waychunas (1989) calls for the generation of additional data to more directly link the divergence of goodness-of-fit parameters to experiments. He is surely aware that such an effort would require a whole new study that, like most experimental work, could take years to complete (in contrast to his simulated spectra that can be generated in a matter of minutes).

I would also like to dispel the concluding paragraph in Waychunas (1989) that implies willingness on my part to neglect signal-to-noise effects in the analysis of experimental data. This is blatantly misleading. The goal of the original paper was simply to determine the standard errors in Mössbauer measurements on minerals; that manuscript was not concerned with the task of distinguishing between signal-to-noise effects. In fact, as Waychunas (1989) has pointed out, it would have been impossible to examine those effects in a strictly experimental study. I have complimented Waychunas on the service performed by his 1986 paper and praised his results for their significance (Dyar, 1986). Certainly, one must attempt to optimize experimental run conditions by consideration of signal-to-noise and experimental effects. However, the experimental work repeatedly demonstrates that the *total* errors involved in the production and interpretation of a Mössbauer spectrum (including, but not limited to, sample preparation, run time, model assumptions, curve-fitting software, signal-to-noise effects, etc.) may still be far greater than those introduced by signal-to-noise errors alone in an average experiment. By using the error bars proposed in the Dyar (1984) paper (± 0.02 mm/s for isomer shift and quadrupole splittings, $\pm 1.5\%$ per peak on area data), experimentalists are already accounting for the total of all the competing sources of error in simple spectra. In more heavily overlapped spectra, the errors are significantly greater, as pointed out by Dollase (1975); experimentalists commonly quote higher errors in such cases (e.g., Dyar and Burns, 1986). Experience has shown that the improvements and correction to models suggested by Waychunas will improve results, but only by small amounts within the commonly used error bars. Surely time is best spent in increasing the experimental data base and building better spectrometers rather than in encouraging use of statistical parameters yielding only minor improvements that are "in the noise" with regard to *total* experimental error.

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