

Critical Evaluation of 'Statistical Best Fits' To Mössbauer Spectra

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Abstract

Computer fitting of the Mössbauer spectrum of a holmquistite has shown that statistical (chi-squared) tests for "best fits" to spectra can give potentially misleading results.

Introduction

Mössbauer spectroscopy is now used widely in the study of minerals. Many mineral spectra typically consist of doublets due to ferrous and ferric iron in different environments. In particular, measurements of peak areas can be used to estimate site populations. Doublet parameters are estimated by computer fitting, and statistical tests are applied to discriminate between fits.

However, statistical tests alone are insufficient. The fitted parameters themselves must be considered. Other evidence, *e.g.*, independently determined site populations, may also be available. Analysis of the spectrum of a holmquistite provides a clear example of the way in which statistical tests may be misleading if applied alone.

Computer fitting and tests of acceptability

The spectrum, of 512 points, was fitted to Lorentzian lineshapes using the program of Stone (1967, and personal communication). The program minimizes the observed residual R_0 , the weighted sum of the squares of the residuals at each spectrum point:

$$R_0 = \sum_{r=1}^{512} w_r [f(x | \bar{q}) - y(x_r)]^2 \quad (1)$$

In Stone's program the weighting factor w_r is the inverse of the square root of the observed count $y(x_r)$ at the r th channel. \bar{q} is the vector of the fitted parameters, which are suitably constrained. The value of R_0 indicates closeness of fit, and is also used for statistical tests.

Counting is subject to random errors. Consequently, even if the spectrum were perfect and the true peak parameters \bar{q}_0 were known, the ideal residual R_i , which is defined as

$$R_i = \sum_{r=1}^{512} w_r [f(x | \bar{q}_0) - y(x_r)]^2 \quad (2)$$

would be non-zero. R_i follows the chi-squared distribution; if a set of fitted parameters \bar{q} is a valid approximation to \bar{q}_0 then R_0 is a value from this distribution. Confusion arises because the function here denoted R_0 is conventionally referred to as " χ^2 " whereas it is R_i , not R_0 , which follows the χ^2 distribution. To test the hypothesis that \bar{q} is a valid approximation to \bar{q}_0 , one uses the percentage points of the χ^2 distribution to assess the probability that R_i would exceed the value R_0 .

For a 512-channel spectrum, the 5 percent, 1 percent and 0.1 percent points of the χ^2 distribution are roughly 540, 570 and 590. That is, the probability is 5 percent that R_i will exceed 540, and so on. Thus if the parameters \bar{q} give $R_0 > 590$, it is highly unlikely that \bar{q} is a valid approximation to \bar{q}_0 . If R_0 decreases to 570, the probability that R_i would exceed R_0 increases tenfold. It is less reasonable to reject the new fit. A fit with R_0 below the 1 percent point will be preferred to one with a higher value. The latter would be rejected statistically and also because a high residual is often associated with a poor visual fit. Usually, high R_0 values are obtained in the early stages of fitting.

It is reasonable to reject a fit with R_0 between the 5 percent and 1 percent points if one with a markedly lower R_0 can be obtained. But below this, statistical tests cannot discriminate. For example, there is quite a high probability that R_i would exceed 520 so there are no *statistical* grounds for preferring a fit with $R_0 = 520$ to one with $R_0 = 540$ (though the '520 fit' will certainly be the closer).

R_0 can be considered reasonable if it lies between the 99 percent and 1 percent points of the χ^2 distribution (*e.g.*, Bancroft, Burns and Stone, 1968). Within these limits, it may be supposed (up to a point) that a closer fit, with a lower R_0 value, is more accurate. However, low R_0 values are also unreason-

TABLE 1. 99% AND 1% POINTS FOR A 512-CHANNEL SPECTRUM

No. of peaks (n)	6	6	6	8	8	8
No. of constraints (n_c)	6	3	0	8	4	0
Degrees of freedom (ν)*	497	494	491	493	489	485
1% point**	425.9	423.1	420.3	422.2	418.5	414.8
99% point **	572.5	569.3	566.1	568.2	563.9	559.6

*The spectrum was fitted to $(3n + 3)$ parameters. Thus the number of degrees of freedom is given as $\nu = 512 - (3n + 3 - n_c)$

**The 99% and 1% points are given by Bancroft, Burns and Stone (1968) as $\nu \pm 3.3 \sqrt{\nu} + 2.2$

able (they may show that the program is fitting spurious peaks to statistical fluctuations in y). There is, for example, only a 1 percent probability that R_i would lie below the 99 percent point of the χ^2 distribution.

Additionally, small improvements in R_0 must be disregarded. Changes in the combination of peaks or constraints produce small changes in the values of the percentage points (Table 1). R_0 follows these even when the fit is not improved (compare Bancroft, Maddock and Burns, 1967).

In the absence of other criteria, when two fits give similar R_0 values, the simpler fit is preferred.

Example and Discussion

The example used here is the spectrum of a holmquistite from Benson pegmatite mine, Mtoko,

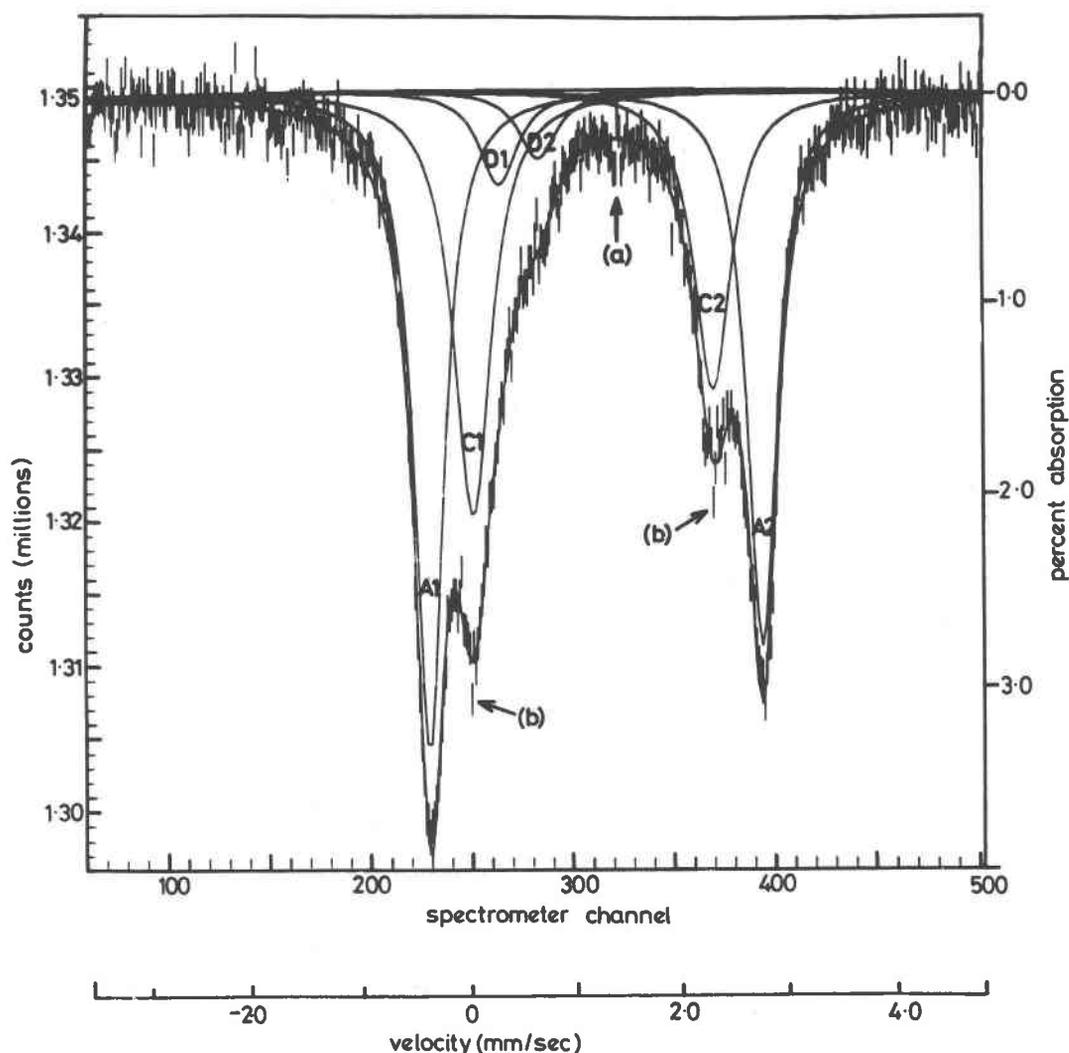


FIG. 1. Mossbauer spectrum of holmquistite, showing the six peak fit. The approximate relationship between velocity and spectrometer channel number is indicated.

(a): indicates a small peak due to a small proportion of Fe in the Al foil used as a radiation filter.

(b): indicates channels which have "dropped out" in the counting process. Both these features will increase R_0 .

TABLE 2. MÖSSBAUER PARAMETERS FOR HOLMQUISTITE: SIX PEAK FIT*

Peak	C.S.	Q.S.	Width**	I ₁ ***	I ₂ ***	I***
A	1.13(1)	2.81(2)	0.30(1)	0.28(1)	0.24(0)	0.52(1)
C	1.11(1)	2.03(2)	0.38(1)	0.23(2)	0.16(1)	0.39(2)
D	0.49(4)	0.33(7)	0.40(6)	0.05(2)	0.04(1)	0.09(2)

*Center Shift (C.S.) and Quadrupole Splitting (Q.S.) values are in mm/sec relative to iron foil. Widths in mm/sec. Areas are normalized. Standard deviations, in parentheses, are in units of the least significant figure. Since only a single spectrum is reported here, the values must be regarded as unconfirmed.

**Widths of components of each doublet constrained equal

***I₁ and I₂ are doublet component intensities (areas). I = I₁ + I₂

Rhodesia (von Knorring and Hornung, 1961). A full report is in preparation.

In the spectrum (Fig. 1) two ferrous iron doublets are clearly resolved. The shoulder at 0.6 mm/sec indicates the presence of a doublet due to ferric iron.

A fit to three doublets A, C and D (Table 2) was obtained with $R_0 = 575.0$. In Figure 1, low and high velocity components are numbered 1 and 2 respectively.

The specimen has $1.45 \text{ Fe}^{2+} + \text{Fe}^{3+}$ per formula unit. The relative doublet intensities therefore give the following assignments (*p.f.u.*): A, $0.75 \pm 0.02 \text{ Fe}^{2+}$; C, $0.57 \pm 0.04 \text{ Fe}^{2+}$; D, $0.13 \pm 0.04 \text{ Fe}^{3+}$ (see note * to Table 2). By comparison with site populations determined for this specimen by Whittaker (1969) using X-ray diffraction (Table 3), doublet A is assigned to *M*(1) sites and C to *M*(3). There is no contribution from Fe^{2+} in *M*(4), whose high distortion would give a clearly resolved doublet with quadrupole splitting around 1.8 mm/sec (Bancroft, Maddock, Burns and Strens, 1966). Doublet C, being broader, would normally be thought to be an unresolved combination of doublets, in this case implying a limited contribution from *M*(2).

Thus the six peak fit can be interpreted in terms of the known details of the holmquistite structure, and the results agree with X-ray measurements. Similar peak parameters are obtained for other silicates (*e.g.*, Bancroft, Maddock and Burns, 1967).

TABLE 3. SITE POPULATIONS IN HOLMQUISTITE FROM X-RAY DIFFRACTION (Whittaker, 1969)

Site	Site Occupancy	Total Fe*
M(1)	0.52 Mg + 0.48 Fe*	0.96
M(2)	0.08 Mg + 0.92 Al	0
M(3)	0.46 Mg + 0.54 Fe*	0.54
M(4)	0.05 Mg + 0.90 Li + 0.03 Na	0
A	0.04 (Ca + K)	0

*As used here, Fe represents $\text{Fe}^{2+} + \text{Fe}^{3+} + \text{Ti} + \text{Mn}$

TABLE 4. MÖSSBAUER PARAMETERS FOR HOLMQUISTITE: EIGHT PEAK FIT*

Peak	C.S.	Q.S.	Width**	I ₁ ***	I ₂ ***	I***
A'	1.13(2)	2.91(3)	0.22(2)	0.12(5)	0.12(4)	0.24(9)
B'	1.12(3)	2.69(5)	0.28(3)	0.17(6)	0.11(5)	0.28(11)
C'	1.11(1)	2.01(2)	0.37(1)	0.24(2)	0.16(1)	0.40(2)
D'	0.49(3)	0.30(7)	0.35(5)	0.04(1)	0.04(1)	0.08(1)

*For notes and explanation, see Table 2

However, a high residual and unequal doublet widths are both normally taken to indicate incomplete resolution (though Burnham, *et al.* [1971] have observed unequal peak widths in spectra of pyroxenes, which have only two *M* sites). An attempt was therefore made to fit a third ferrous doublet. This raised the question of statistical tests for best fits.

The best eight peak fit (Table 4) was fairly highly constrained. The residual was considerably improved to 536.7, which is a statistically significant improvement and also indicates a closer fit. But the fit cannot be accepted for this reason alone. Thus a comparison of the parameters for the six and eight peak fits (Tables 2 and 4) shows that it is doublet A of the six peak fit which has been decomposed, giving A' + B', rather than the broader doublet C. The parameters of C and C' are identical within the quoted standard deviations. Further, the width of A' is now unreasonably small and A' and B' overlap closely and thus are unlikely to be completely resolved. They may well represent inaccurate resolution of peaks whose real widths are much more nearly equal (and whose intensities are therefore less nearly equal). In any case, the attempt to achieve more uniform peak widths has failed. Secondly, the relative peak areas give the assignments (*p.f.u.*): A', $0.34 \pm 0.13 \text{ Fe}^{2+}$; B', $0.41 \pm 0.15 \text{ Fe}^{2+}$; C', $0.58 \pm 0.04 \text{ Fe}^{2+}$; D', $0.11 \pm 0.02 \text{ Fe}^{3+}$. At first sight, this would indicate a distribution of Fe^{2+} over three sites, presumably *M*(1), *M*(2) and *M*(3). If the assignment of C, and therefore of C', to *M*(3) holds, then A' and B' must be assigned to *M*(1) and *M*(2) (not necessarily respectively). The eight peak fit then indicates a rather even distribution of Fe^{2+} over *M*(1) and *M*(2). This directly contradicts the X-ray result, *i.e.*, that iron is confined to *M*(1) and *M*(3), whereas the six-peak fit seemed to confirm the X-ray result.

Thus there is justification for preferring the six-peak fit and its interpretation, though from statistical arguments alone it would seem to be the less acceptable. The eight peak fit must have some less obvious

interpretation. For example, A' and B' may correspond to iron in $M(1)$ sites with distinctly different next-nearest neighbors, or the true lineshapes may deviate from the ideal Lorentzian for several reasons. A similar pair of doublets, due to ferric iron, has been observed by Dowty (1971) in garnet spectra.

However, a detailed interpretation is not attempted here. The intention is to point out the dangers of an uncritical use of the " χ^2 " test, which must be borne in mind when fitting complex spectra of minerals. In the example quoted, the uncritical acceptance of a statistically preferable fit would have led to an incorrect interpretation. In another case, this might equally well be true, and false conclusions might be drawn, especially if other evidence (*e.g.*, from X-ray diffraction) was not available.

It is essential to apply other considerations, and some of those used here—study of the fitted spectrum, peak widths, parameter deviations, *etc.*—will be of general use. Statistical tests for the acceptability of fits must be applied critically and not given undue weight.

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