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A Simple Unified Equation for Accurate and Rapid Quantification of $Fe^{3+}/\Sigma Fe$ Obtained from Room Temperature Mössbauer Spectroscopic Measurements

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Abstract

The accurate quantification of $\frac{Fe^{3+}}{\Sigma Fe}$ ratios for Mössbauer spectroscopic room temperature measurements involves many steps and, when shown in a composite Mössbaur data table, does not allow enough space for more Mössbauer parameters to be presented in the composite table. So a simple formula is derived, (presented as a short communication) which users will find helpful when they have to determine corrected $\frac{Fe^{3+}}{\Sigma Fe}$ ratios in their room temperature Mössbauer experiments.

Key words: Mössbauer spectroscopy, Recoilless fractions**,** Corrected $\frac{Fe^{3+}}{\Sigma Fe}$ ratios, Room temperature measurements

Introduction

The recoilless fractions f_2 and f_3 of Fe^{2+} and Fe^{3+} ions in tetrahedral and octahedral sites, respectively, are not equal and are also temperature dependent. This imposes some limitations

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on the Mossbauer technique when measurements are made at room temperature. In fact, inaccuracies of overestimation as high as 25% have been reported for $\frac{Fe^{3+}}{\Sigma Fe}$ ratios obtained from room temperature Mössbauer measurements [1].

The correction needed involves many steps and, when included in a composite Mössbauer data table, does not allow enough space for major Mössbauer parameters.

However, the equation 5 below, when used to calculate corrected $\frac{Fe^{3+}}{\Sigma Fe}$, would not only alleviate this problem but also help calculations to be carried more quickly, especially when many samples are being analyzed.

Derivation of the formula

Starting from a dimensionally correct expression similar to the one obtained in [1, 2]

$$\left(\frac{Fe^{3+}}{\Sigma Fe}\right)_{corrected} = \frac{f_2}{f_3}\left(\frac{Fe^{3+}}{Fe^{2+}}\right)_{observed\ \ measurement} * \left(\frac{Fe^{2+}}{\Sigma Fe}\right)_{corrected} \qquad 1$$

where f_2 and f_3 are correction factors for Fe^{2+} and f^{3+}, respectively, in a clean single crystal Mössbauer sample.

Equation 1 can be written as

$$\left(\frac{Fe^{3+}}{\Sigma Fe}\right)_{corr} = \frac{1}{C}\left(\frac{Fe^{3+}}{Fe^{2+}}\right)_{ob\_ms} * \left(\frac{Fe^{2+}}{Fe^{2+}+Fe^{3+}}\right)_{corr} \qquad 2$$

Where $C=f_3/f_2$

$$\left(\frac{Fe^{3+}}{\Sigma Fe}\right)_{corr} = \frac{1}{C}\left(\frac{Fe^{3+}}{Fe^{2+}}\right)_{ob\_ms} * \left(\frac{1}{1+\frac{Fe^{3+}}{Fe^{2+}}}\right)_{corr} \qquad 3$$

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$$= \frac{1}{C}\left(\frac{Fe^{3+}}{Fe^{2+}}\right)_{ob\_ms} * \left[1 - \left(\frac{\frac{Fe^{3+}}{Fe^{2+}}}{1 + \left\{\frac{Fe^{3+}}{Fe^{2+}}\right\}}\right)_{corr}\right]$$

$$= \frac{1}{C}\left(\frac{Fe^{3+}}{Fe^{2+}}\right)_{ob\_ms} * \left[1 - \left(\frac{Fe^{3+}}{\Sigma Fe}\right)_{corr}\right]$$

$$= \frac{1}{C}\left(\frac{Fe^{3+}}{Fe^{2+}}\right)_{ob\_ms} - \frac{1}{C}\left(\frac{Fe^{3+}}{Fe^{2+}}\right)_{ob\_ms} * \left(\frac{Fe^{3+}}{\Sigma Fe}\right)_{corr}$$

$$\therefore \left(\frac{Fe^{3+}}{\Sigma Fe}\right)_{corr} * \left[1 + \frac{1}{C}\left(\frac{Fe^{3+}}{Fe^{2+}}\right)_{ob\_ms}\right] = \frac{1}{C}\left(\frac{Fe^{3+}}{Fe^{2+}}\right)_{ob\_ms}$$

Hence

$$\left(\frac{Fe^{3+}}{\Sigma Fe}\right)_{corr} = \frac{\frac{1}{C}\left(\frac{Fe^{3+}}{Fe^{2+}}\right)_{ob\_ms}}{1 + \frac{1}{C}\left(\frac{Fe^{3+}}{Fe^{2+}}\right)_{ob\_ms}} \qquad 4$$

The r.h.s. of eqn 4 can be written as: $1 - \frac{1}{\left[1 + \frac{1}{C}\left(\frac{Fe^{3+}}{Fe^{2+}}\right)_{ob\_ms}\right]}$

Finally, the required equation can therefore be written as:

$$\left(\frac{Fe^{3+}}{\sum Fe}\right)_{Corr} = 1 - \frac{1}{\left[1 + \frac{1}{C}\left(\frac{Fe^{3+}}{Fe^{2+}}\right)_{ob\_ms}\right]} \qquad 5$$

Conclusion

The *r.h.s.* of equation 5 can be written into the *Excel spreadsheet function-box* as:

= (1-(1/(1+(C_o*R))))

where $C_o = f_2/f_3$; and R refers to the cell into which the value of the calculated observed (Fe^{3+}/Fe^{2+}) ratio is located in the spreadsheet.

Alternatively, if Fe^{3+}/Fe^{2+} are not calculated beforehand, then the expression to be put in the Excel function box is: =(1-(1/(1+(Co*(X3/X2)))))

where, X_1 and X_2 refer to the cells into which the values of the observed Fe^{3+} and Fe^{2+}, respectively, are located in the spreadsheet.

Example: For clean single crystal chromites, the values reported in [3] for f_2 and f_3 are 0.687 and 0.887, respectively. Therefore, C =1.291, i.e. (C_o= 1/C=0.7745)

If the corrected ($Fe^{2+}/\Sigma Fe$ is required, then Fe^{2+} and Fe^{3+} in the formula can be interchanged and, C is then f_2/f_3.

The formula given in equation 5 has been tested many times and the results obtained are consistent when compared with LN temperature measurements results when chi squared is in acceptable range, $0.95 < \chi^2 < 1.5$. It is also very useful, especially if many samples are to be analyzed.

References

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