

# Assessing the use of <sup>7</sup>Li MAS NMR Spectral Simulations for the Characterization of Disorder in Lithium Containing Materials

Todd M. Alam<sup>1\*</sup>, Sarah K. McIntyre<sup>1</sup>, Emily Baldwin<sup>1</sup>, Amy Garner<sup>1</sup> and May Nyman<sup>2</sup>

<sup>1</sup>NMR Laboratory, Department of Electronic and Nanostructured Materials, and

<sup>2</sup>Department of Geochemistry, Sandia National Laboratories, Albuquerque, NM

## Introduction

Solid state NMR of quadrupolar nuclei continues to be important for the characterization of inorganic materials. A benefit of solid state NMR is the ability to study amorphous systems or materials that do not exhibit perfect long range order. In addition, NMR can readily measure and quantify distributions of the local nuclear environment that are present in these disordered materials. Recently, several examples that determine local interaction distributions through analysis of either static and MAS NMR second-order quadrupolar line shapes have been reported, with these methods being incorporated in the DMFIT and QuadFit simulation programs [1,2]. Unfortunately, the application of these second-order quadrupolar line shape methods to systems with very small quadrupolar interactions, such as <sup>7</sup>Li containing materials, have not been discussed. For <sup>7</sup>Li (I = 3/2) MAS NMR the quadrupolar interaction is typically small (< 100 kHz), with both the static and MAS NMR line shape exhibiting only first order quadrupolar perturbations. In the previous quadrupolar distribution examples, distinct variations in the second order quadrupolar line shape of the central transition were utilized in the analysis of the distribution of the quadrupolar interaction. These dramatic line shape variations are not typical of <sup>7</sup>Li where the MAS NMR spectra are composed of a relatively narrow central transition resonance and a series of sidebands arising from the 3/2 ↔ 1/2 satellite transitions. Luckily the shape of the satellite envelope varies with the strength and symmetry of the quadrupolar interaction, and therefore may provide a means to measure the quadrupolar interaction distribution. In this poster, we explore the use of <sup>7</sup>Li MAS NMR spectral line shape analysis to determine quadrupolar interactions.

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## Distribution Models

Following the formalism of reference [4] the spectral line shape is given as the summation over all nuclei and local environments and is described by a probability density function (PDF) using

$$S(\nu) \sim \int p_{\Omega_Q}(\Omega_Q) \delta[\nu - \nu(\Omega_Q)] d\Omega_Q$$

Assuming no correlation between the powder average orientation and the eigenvalues of the electrical field gradient the PDF can be written as a combination of the powder average summation and the weighted average of the individual ( $\nu_Q, \eta$ ) powder line shapes.

$$p_{\Omega_Q}(\Omega_Q) = p_{\text{angles}}(\alpha, \beta, \gamma) p_Q(\nu_Q, \eta)$$

$$S(\nu) \sim \int_{-\infty}^{\infty} \int_0^1 p_Q(\nu_Q, \eta) \left\{ \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} \frac{1}{8\pi^2} \delta[\nu - \nu(\Omega_Q)] \sin \beta d\beta d\alpha d\gamma \right\} d\eta d\nu_Q$$

$$S(\nu) \sim \sum_{\nu_Q} \sum_{\eta} p_Q(\nu_Q, \eta) S(\nu_Q, \eta)$$

The PDF of the ( $\nu_Q, \eta$ ) random variables is described as either independent Gaussians (4 variables), which has been argued to be not physically founded, or as the joint Czjzek model PDF (1 variable) [3,4].

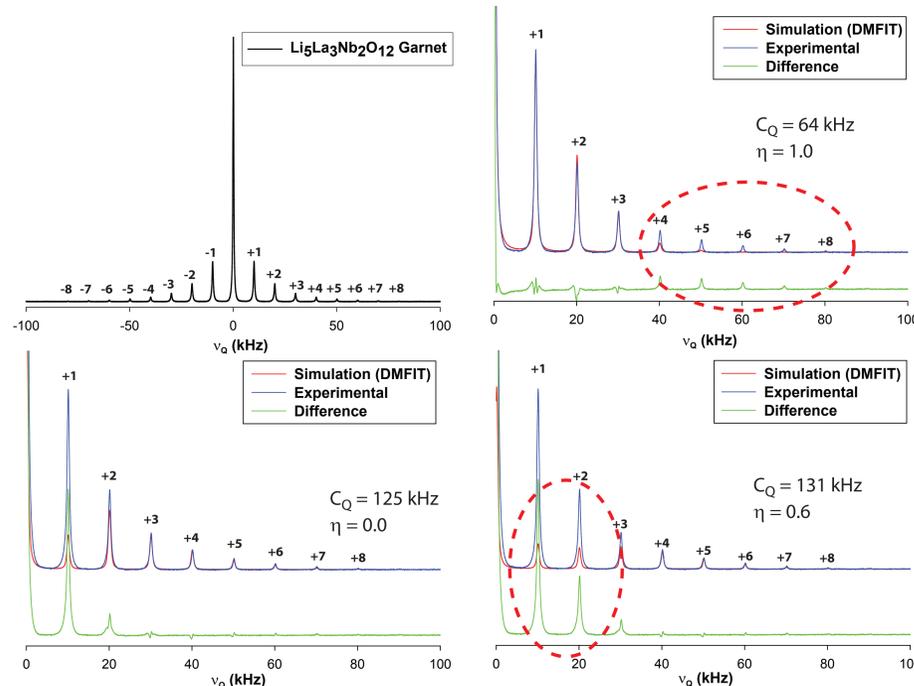
### Combined Gaussian Distributions

$$p_Q(\nu_Q, \eta) = p(\nu_Q) p(\eta) = \frac{1}{2\pi\sigma_{\nu_Q}\sigma_{\eta}} \exp\left[-\frac{(\nu_Q - \bar{\nu}_Q)^2}{2\sigma_{\nu_Q}^2}\right] \exp\left[-\frac{(\eta - \bar{\eta})^2}{2\sigma_{\eta}^2}\right]$$

### Czjzek Model Distribution

$$p_Q(\nu_Q, \eta) = \frac{1}{\sqrt{2\pi}\sigma} \nu_Q^3 \left(1 - \frac{\eta^2}{9}\right) \exp\left[-\frac{\nu_Q^2 \left(1 + \frac{\eta^2}{3}\right)}{2\sigma^2}\right]$$

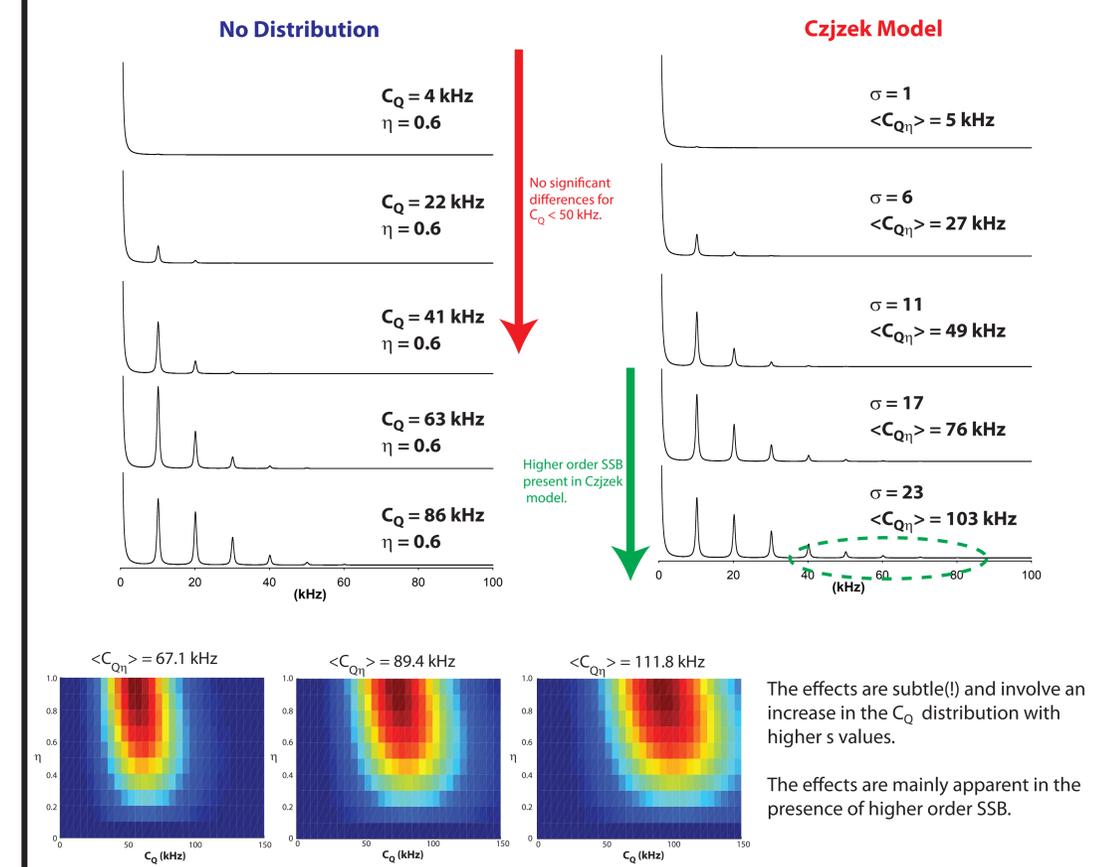
## <sup>7</sup>Li MAS NMR Analysis Issues



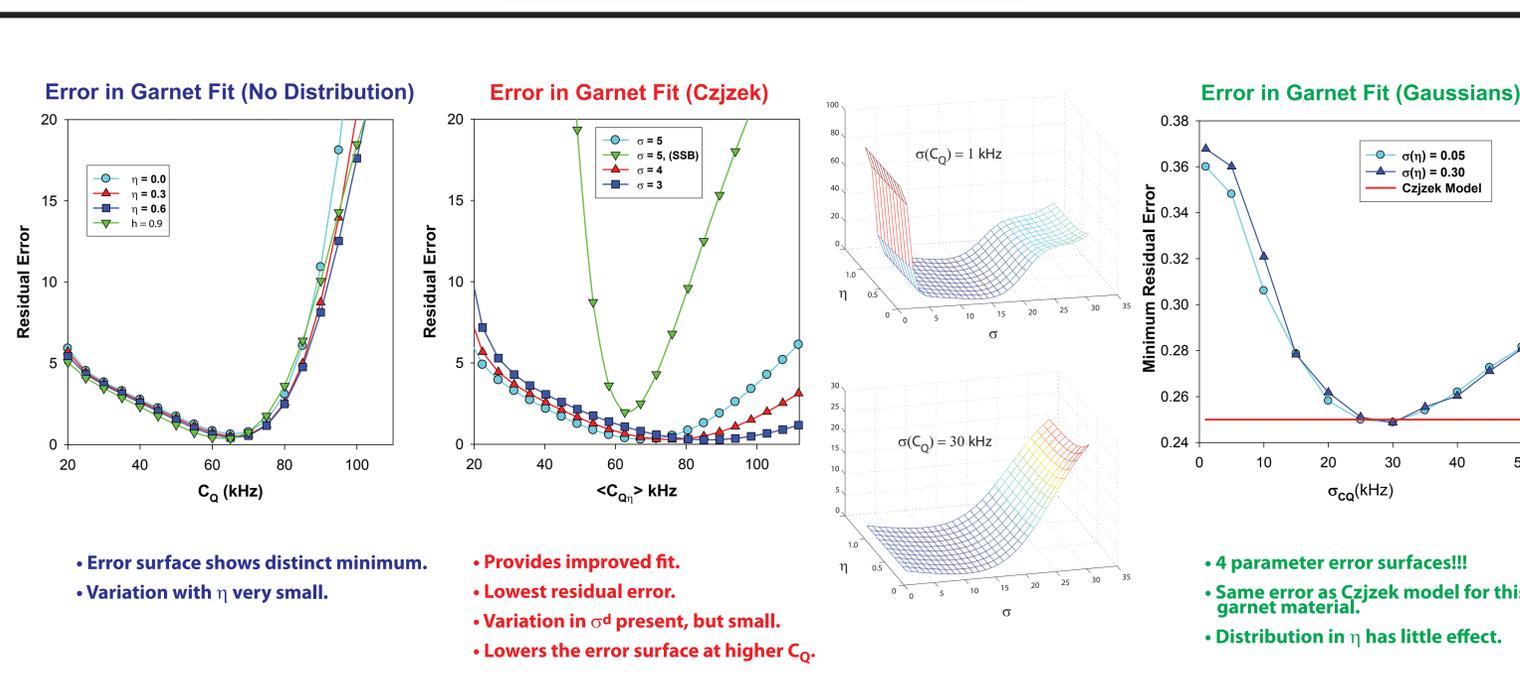
We experimentally encountered <sup>7</sup>Li MAS NMR spectra for materials that are not simulated correctly using a single  $C_Q$  and  $\eta$  value for the quadrupolar interaction. As an example, consider the nanocrystalline garnet powder material shown above. In addition to the central transition, there are 16 spinning sidebands (SSB) observable in the MAS NMR spectra. Simulations that concentrate on the inner SSB (+1 to +3) underestimate the magnitude of  $C_Q$ , while simulations that reduce the error of the outer SSB fail to correctly predict the relative intensity of the inner SSB. Note large differences in values!

**Does including distribution for the quadrupolar interaction improve simulations?**

## Model Line Shape Variations



## Error Surfaces



• Error surface shows distinct minimum.  
• Variation with  $\eta$  very small.

• Provides improved fit.  
• Lowest residual error.  
• Variation in  $\sigma$  present, but small.  
• Lowers the error surface at higher  $C_Q$ .

• 4 parameter error surfaces!!!  
• Same error as Czjzek model for this garnet material.  
• Distribution in  $\eta$  has little effect.

## Conclusions

• Including distribution improved the spectral line shape fits for some materials.

• The Czjzek model can easily be incorporated and allows distributions to be described by a single parameter -  $\sigma$ .

• The impact of the Czjzek distribution is not significant until  $\sigma > 10$  ( $C_Q \sim 50$  kHz).

• Similar errors observed between the Czjzek model and Gaussian distributions in both  $C_Q$  and  $\eta$ .

• The Gaussian and Czjzek models are not distinct for the materials studied to date.

• Other distributions are possible in some examples, i.e. bi-modal.

• Distributions may be a dynamic averaging effect.

### References

[1] T.F. Kemp, M. E. Smith, Solid State NMR, 35, 243-252 (2009). [2] D. Massiot et al., Magnetic Resonance Chemistry, 40, 70-76 (2002). [3] G. Czjzek et al., Phys. Rev. B, Condens. Matter, 23, 2513-2530 (1981). [4] J.-B. d'Espinose de Lacaillerie, C. Fretigny, D. Massiot, J. Magnetic Resonance, 192, 244-251 (2008).