

VOIGT—BASED METHODS FOR ARBITRARY SHAPE QUADRUPOLE SPLITTING DISTRIBUTIONS (QSD's) APPLIED TO QUASI—CRYSTALS

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It is now well established that, as with amorphous alloys, the Mössbauer spectra of icosahedral alloys exhibit QSD's. This is evidence for intrinsic local disorder present in icosahedral structures. The shapes of the QSD's have not been unambiguously established and, as a result, it has been difficult to link these shapes with other physical properties of these novel and complex alloys. We apply a recently developed arbitrary shape static hyperfine parameter distribution method to the case of a new icosahedral alloy series: $\text{Al}_{65}\text{Cu}_{20}\text{Cr}_{15-x}\text{Fe}_x$. The method proves to be a powerful and useful tool in this application. It enables us to evaluate several robust features and to identify other features that are subject to large uncertainties due to extreme sensitivity to details.

Powerful Voigt-based methods for arbitrary shape QSD's and hyperfine field distributions (HFD's) have recently been developed /1/. These have so far only been applied to HFD's where they exhibit clear advantages compared to other methods, due to the correctness of assuming that the true HFD can be represented by a sum of Gaussian components /1,2/.

It is intuitively obvious that any physical arbitrary shape distribution can be expressed as a sum of Gaussian components. For a QSD, we write:

$$P(\Delta) = \sum_{i=1}^N \rho_i G_i(\Delta_{oi}, \sigma_{\Delta i}; \Delta) \quad (1)$$

where each Gaussian G_i is normalized to an area of 1, has a center at Δ_{oi} and has a width $\sigma_{\Delta i}$. ρ_i is a weight factor and $\sum \rho_i = 1$. N is the chosen number of components.

To the extent that the true QSD is Gaussian-like, $N = 1$ will already give a fair representation of the spectrum. Of course, each elemental doublet also has a center shift δ that is taken to be related to the quadrupole splitting ($QS \equiv \Delta$) by:

$$\delta = \delta_0 + \delta_1 \Delta. \quad (2)$$

It follows /1/ that the lineshape is a sum of $2N$ Voigt lines:

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$$Q(\nu) = \sum_{i=1}^N \rho_i \sum_{k=\pm 1} V_{ik}(\delta_o + \delta_1 \Delta_{oi} + k\Delta_{oi}/2, |\delta_i + \frac{k}{2}| \sigma_{\Delta i}, \gamma, h_k; \nu) \quad (3)$$

where γ is the elemental Lorentzian FWHM and h_k are the elemental Lorentzian heights for low ($k = -1$) and high ($k = +1$) energy components. For a perfect powder, neglecting thickness effects, and in the absence of the Goldanski-Karyagin effect, $h_- = h_+$.

We have made a detailed comparison of this method with both the shell model and the Hesse-Rübartsch/LeCaer-Dubois method /3/. We find that the shell model imposes a restricted QSD shape that in turn gives rise to a questionable δ - Δ coupling requiring a large quadratic term (i.e. $\delta \Delta^2$). The Hesse-Rübartsch/LeCaer-Dubois method gives rise to spurious structure in the form of oscillations in $P(\Delta)$ that are overly sensitive to details such as the exact assumed values of γ .

In this paper, we restrict ourselves to illustrating how well a single Gaussian component ($N = 1$) Voigt-based analysis is able to model the room temperature spectra of the quasi-crystal series $Al_{65}Cu_{20}Cr_{15-x}Fe_x$ with $x = 0.075, 3, 6, 9, 12,$ and 15 .

The samples were prepared using a single roller melt-spinning apparatus. They are single phase within the sensitivity of standard X-ray diffraction, except the $x = 9$ composition that contains an unidentified second phase. The absorber thicknesses were in the range 0.005-0.087 mg $^{57}Fe/cm^2$. All δ 's are given relative to α -Fe at room temperature.

The $N = 1$ fit results are given in Table 1. Since we impose $h_- = h_+$, the two Voigt lines in a given spectrum (Eq.3) have equal areas by design. Three representative fitted spectra are shown in Fig.1 with difference spectra. The number of free parameters, including a flat BG, is 7; the same number as would be required by two individual Lorentzian lines with a flat BG. Such Lorentzians give much poorer (and unphysical) fits.

Table 1. $N = 1$ fit results for $Al_{65}Cu_{20}Cr_{15-x}Fe_x$.

x at. %	σ_{Δ} mm/s	Δ_o mm/s	δ_o mm/s	δ_1	γ mm/s	χ_{red}^2
0.075	0.180	0.585	0.284	-0.110	0.279	2.9
3	0.199	0.508	0.243	-0.026	0.221	0.8
6	0.208	0.505	0.262	-0.049	0.214	1.4
9	0.200	0.453	0.256	-0.041	0.226	2.3
12	0.184	0.397	0.245	-0.016	0.239	5.8
15	0.176	0.365	0.235	+0.016	0.237	4.6

As indicated by the reduced chi-squared (χ_{red}^2) and by the fits themselves, the fit to the $x = 3$ spectrum is ideal ($\chi_{red}^2 \sim 1$) whereas those for $x = 6$ and 9 are almost ideal and the fits for $x = 0.075, 12,$ and 15 are statistically unsatisfactory.

Indeed, the $x = 3$ fit (Fig.1) is a good example of a case where a single Gaussian QSD gives a perfect fit. Allowing more free

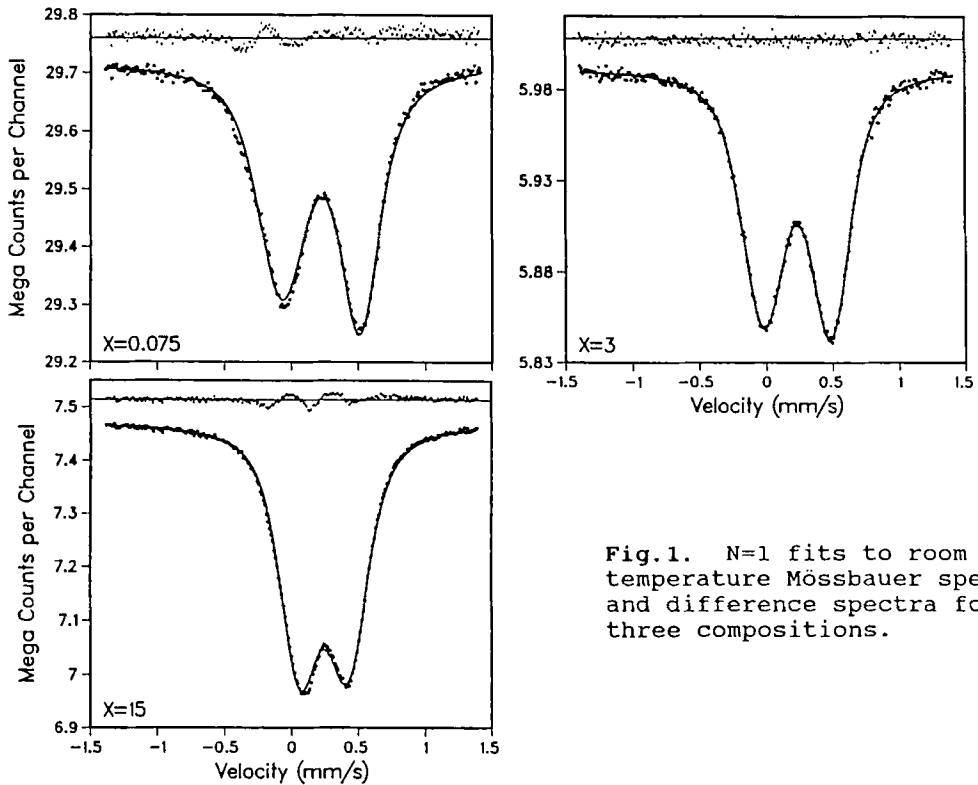


Fig.1. N=1 fits to room temperature Mössbauer spectra and difference spectra for three compositions.

parameters, or using a QSD method that allows more structure than that of a simple Gaussian, would not be justified. Any such structure should be considered suspect and artificial. More structure may exist in the true QSD. Unfortunately, the true QSD does not follow uniquely from the spectrum /3/.

The misfits occurring at compositions $x \neq 3$ are qualitatively the same. They are associated to the low-velocity absorption lines where they correspond to "doublets" in the difference spectra (e.g. $x = 0.075$, Fig.1; at -0.03 and -0.38 mm/s). These differences cannot be attributed to impurities since they closely follow the associated absorption lines (e.g. $x = 15$, Fig.1; the difference "peaks" here are at $+0.13$ and -0.18 mm/s). Such different patterns occur with various intensities at all compositions $x \neq 3$ and may be intrinsic components of the true quasi-crystal spectra. It is just such features that give $N > 1$ structure in extracted QSD's /3/.

The low-velocity difference peak (e.g. at -0.38 mm/s, $x = 0.075$) always corresponds to a visible shoulder on the low-velocity side of each low-velocity doublet absorption line. Only such visible spectral features can give rise to true features in the QSD's. QSD oscillations and bumps that are not required by either observed spectral features or the particular spectral shape cannot be believed. With featureless spectra, many different QSD's give equivalent statistically acceptable fits. True spectral features seen in high-quality spectra significantly reduce this number of "allowed" QSD's and eliminate entire categories of distributions.

Our fitting model is the simplest model (with the fewest free parameters) that gives near-ideal fits to several alloys in our series

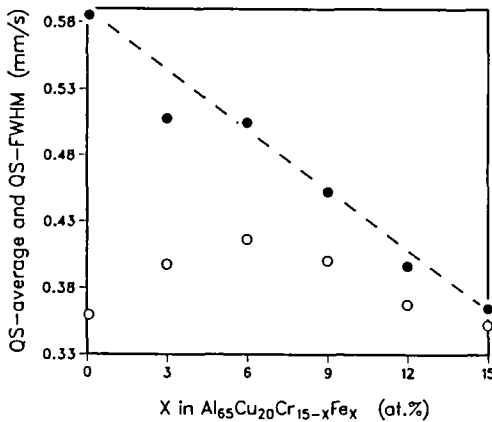


Fig.2. Average QS (filled circles) and FWHM of the QSD (open circles) as functions of x . The dashed line is Eq.(4).

and shows the main compositional trends.

These trends are apparent in the spectra themselves (Fig.1). As x is increased the low-velocity absorption line becomes relatively narrower and deeper and the average QS decreases.

The average QS and the FWHM of the QSD are shown versus x in Fig.2. Apart from the $x = 3$ point, the average QS closely follows a linear decrease given by:

$$\langle \text{QS}(\text{mm/s}) \rangle = 0.59(1) - 0.0151(7) \cdot x(\text{at.}\%) \quad (4)$$

The distribution width, on the other hand, does not decrease monotonically with x but is relatively constant (Fig.2).

Any model for the structure and positions of Fe in this quasi-crystal system will have to be consistent with these trends.

From the fit results given in Table 1, we also conclude that, for all x , the average RT center shift (relative to α -Fe at RT) is $\langle \delta \rangle = +0.235(3)$ mm/s, $\delta_0 = +0.25(1)$ mm/s, and the δ - Δ coupling parameter is $\delta_1 = -0.03(1)$. Also γ always converges to ~ 0.24 mm/s, giving us good confidence in our method.

Ongoing work /3/ accounts for the above mentioned spectral misfits by allowing $N > 1$ QSD structure. The robustness of resulting additional QSD features is being examined. The results presented here (e.g. Fig.2) are not significantly affected by this fine tuning.

In conclusion, the new QSD method /1/ works well. It has the significant advantage over other methods of only allowing as much QSD structure as is required by the spectra (by increasing N gradually until statistically acceptable fits are obtained). Artificial oscillations are avoided by design. With $N = 1$ rapid convergence to unique solutions was obtained.

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