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LETTER

Letter: Comment on the intensities of inelastic neutron scattering spectra

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In a recent paper[1] convincing evidence is given for low temperature symmetry lowering in an exchange-coupled Fe(III) trimer which shows strict three-fold symmetry at room temperature. By using incoherent inelastic neutron scattering (IINS) data, the authors were able to demonstrate that the clusters divide into two equally populated sets of distorted trimers between $T = 300$ and $T = 1.5$ K. The distortion present in each of these two forms is discussed and reference is made to atomic displacements which may be consistent with the observed exchange interactions. This letter concerns the analysis of the IINS data and aims to improve the agreement between the observed and calculated spectra with respect to the intensities of the spectral features.

The IINS spectra were analysed using spin-only models which have previously been shown to accurately model the exchange interactions in similar systems.[2] However, whilst a good agreement was found with the positions of spectral features (the model very accurately reproduces all eight peak positions to within experimental error) the intensities reported in Fig. 2 (reproduced below, Fig. 1) are far from satisfactory. In contrast, a previous study[2c] in which related Fe(III) trimeric systems were modelled, both the peak positions and the intensities were accurately reproduced.

The intensity of a magnetic feature in an IINS spectrum is the product of several factors and is conventionally defined in terms of a partial differential cross section (pdcs) with respect to both energy and solid angle.[3] For such trimer systems, it has been shown to simplify to eqn. (1)[2] where I is the transition

$$d^2\sigma/d\Omega dE' \propto \boldsymbol{k}'/\boldsymbol{k}\cdot F^2(\boldsymbol{Q})\cdot I(1 - \sin(\boldsymbol{Q}R)/\boldsymbol{Q}R) \qquad (1)$$

matrix element and R is the iron–iron separation within the clusters.[2] This approximation in I assumes an equal spacing between all neighbouring Fe(III) sites, but has been shown to be valid for systems displaying small distortions away from three-fold symmetries.[2] Therefore, for an accurate comparison of IINS data to theory-based spectra the full pdcs expression must be determined for the calculated points in order to have any physical relevance to the experimentally measured features.

The $\boldsymbol{Q}$-dependence of the MARI data is referred to in the paper, but no information is given concerning the range of $\boldsymbol{Q}$-values covered in Fig. 2. However, we have calculated the excitation surface over all of the available $\boldsymbol{Q}$ and $h\omega$–space available to the high angle detector bank ($2\theta = 13$–$135°$) of MARI[4] at $E_i = 25$ meV, with $R = 3.317$ Å.[1] In the absence of the precise experimental data range, a simple sum over all angles across this surface was then performed to obtain a model spectrum in $h\omega$ which very accurately models the experimental intensities, Fig. 2. The root mean squared difference between the measured and observed intensities is found to decrease by 30% following the present treatment, Table 1. The accuracy of the agreement is largely limited by both the undetermined nature of the background, assumed in this analysis to be continuous and smoothly decaying and the absence of all information pertaining to the precise spectral range reported. On a qualitative basis, the overall appearance of the revised model spectrum more closely resembles the measured case.

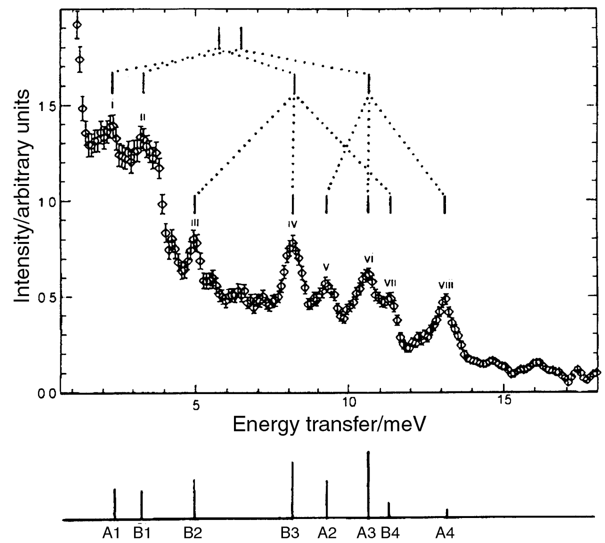

Fig. 1 IINS spectrum of $[Fe_3O(O_2CPh)_6(py)_3]ClO_4\cdot py$ reproduced from ref. 1.

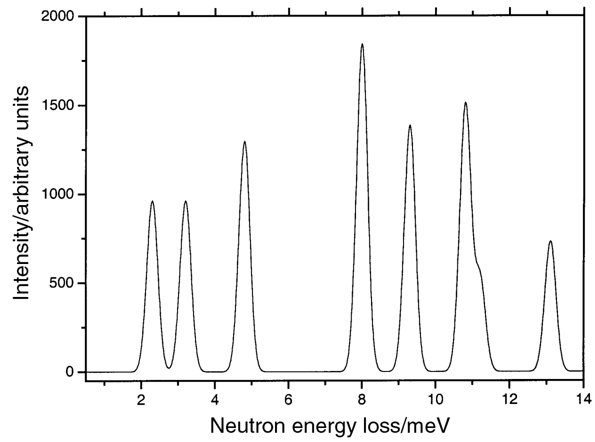

Fig. 2 Calculated IINS spectrum for the coupling model proposed in ref. 1, calculated as a sum over all angles between 13 and 135° for an incident energy of 25 meV.

An additional consideration is that band viii was calculated to be less intense than the measured case in both the original paper and here (viii = 0.38 × iv herein and 0.11 × iv in ref. 1). A closer inspection of this spectral feature suggests that a phonon band ($\nu \approx 100$ cm^{-1}) lies below the magnetic contribution; an approximate deconvolution of the two provides a good agreement with the present model. The existence of a phonon feature in this spectral region may be verified by the

Table 1 Comparison of observed and calculated IINS intensities, normalised to the most intense measured feature

Energy/meV	Band	Measured	Present work	Ref. 1
2.3	i	0.77	0.63	0.53
3.4	ii	1.23	0.63	0.53
4.9	iii	0.69	0.75	0.74
8.2	iv	1.0	1.0	1.0
9.35	v	0.62	0.69	0.63
10.65	vi	0.77[a]	0.78	1.16
11.35	vii	0.31[a]	0.28	0.26
13.15	viii	0.39[a]	0.38	0.11

[a] Approximate deconvolution.

considering evolution of band viii as a function of $\boldsymbol{Q}$ in the original experimental data.

Hence, by performing a rigorous evaluation of the calculated spectrum, the agreement between the observed and theory-derived spectra more closely mirrors that previously found in related systems[2] and the relevance of the proposed model of exchange coupling to the system under study is enhanced.

References

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3 For example: G. L. Squires, *Introduction to the Theory of Thermal Neutron Scattering*, Cambridge University Press, Cambridge, 1978.

4 http://www.nd.rl.ac.uk/excitations/mari/