Experimentally determining the exchange parameters of quasi-two-dimensional Heisenberg magnets

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Abstract. Though long-range magnetic order cannot occur at temperatures $T > 0$ in a perfect two-dimensional (2D) Heisenberg magnet, real quasi-2D materials will invariably possess nonzero inter-plane coupling $J_\perp$ driving the system to order at elevated temperatures. This process can be studied using quantum Monte Carlo calculations. However, it is difficult to test the results of these calculations experimentally since for highly anisotropic materials in which the in-plane coupling is comparable with attainable magnetic fields $J_\perp$ is necessarily very small and inaccessible directly. In addition, because of the large anisotropy, the Néel temperatures are low and difficult to determine from thermodynamic measurements. Here, we present an elegant method of assessing the calculations via two independent experimental probes: pulsed-field magnetization in fields of up to 85 T, and muon-spin rotation.

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We successfully demonstrate the application of this method for nine metal–organic Cu-based quasi-2D magnets with pyrazine (pyz) bridges. Our results suggest the superexchange efficiency of the \([\text{Cu}(\text{HF}_2)(\text{pyz})_2]X\) family of compounds (where X can be \(\text{ClO}_4\), \(\text{BF}_4\), \(\text{PF}_6\), \(\text{SbF}_6\) and \(\text{AsF}_6\)) might be controlled by the tilting of the pyz molecule with respect to the 2D planes.

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#### 1. Introduction

Systems that can be described by the \(S = \frac{1}{2}\) two-dimensional (2D) square-lattice quantum Heisenberg antiferromagnet model [1]–[3] continue to attract considerable experimental [4, 5] and theoretical [6]–[9] attention. Recent impetus has been added to this field by suggestions that antiferromagnetic fluctuations from \(S = \frac{1}{2}\) ions on a square lattice play a pivotal role in the mechanisms for superconductivity in the ‘high \(T_c\)’ cuprates [3], [10]–[14] and other correlated-electron systems [15]; moreover, 2D Heisenberg magnets have been suggested as possible test-beds for processes applicable to quantum computation [4, 9].

Although long-range magnetic order cannot occur above \(T = 0\) in a true 2D Heisenberg system [2, 16], real materials that contain planes approximating to 2D Heisenberg systems [2, 4, 17, 18] inevitably possess inter-plane coupling that can lead to a finite Neél temperature [4, 17, 19]. In this context, synthesis of coordination complexes containing ions such as \(\text{Cu}^{2+}\), neutral bridging ligands [4] and coordinating anion molecules [17, 18] has proved fruitful in the production of a variety of 1D and 2D magnetic systems [17], [20]–[22]. The current paper describes high-field magnetization measurements on nine Cu-based (\(\text{Cu}^{2+}\), \(S = 1/2\)) quasi-2D Heisenberg magnets that employ pyrazine (pyz) as a neutral bridging ligand [17, 18]\(^8\). The data show that the field \((B)\)-dependent, low-temperature magnetization \(M(B)\) shows a characteristic sharp ‘elbow’ feature at the transition to saturation, with a concave curvature at lower \(B\). Monte Carlo evaluations of a 2D Heisenberg square lattice with an additional inter-plane exchange coupling energy \(J_\perp\) reproduce the data quantitatively; the degree of concavity depends on the effective dimensionality of the system, while the field at which the ‘elbow’ occurs is an accurate measure of the in-plane exchange energy \(J\). Using these

\(^8\) Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) No. 636104; 683410–683415. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2-1EZ, UK. Fax: +44-1223-336033; \text{http://www.ccdc.cam.ac.uk/conts/retrieving.html}.
Table 1. The quasi-2D magnets studied in this work, along with their saturation fields \( B_c \) and \( g \)-factors (here pyz is pyrazine, pyo is pyridine-N-oxide). Data for oriented single crystals are indicated by \( B_\parallel \) (\( B \) parallel to 2D layers) and \( B_\perp \) (\( B \) perpendicular to 2D layers); other data are for powders. In the latter cases, an average \( g \) was evaluated from single-crystal electron paramagnetic resonance (EPR) data using standard formulae \([25]\). The in-plane exchange energy is calculated using equation \((2)\); typical uncertainties in the values of \( J \) resulting from uncertainties in \( g \) and \( B_c \) are \( \pm0.1 \) K. Neél temperatures \( T_N \) were measured to \( \pm0.04 \) K using \( \mu \)SR \([22]\), apart from \( \text{Cu(pyz)}_2(\text{ReO}_4)_2 \), where the transition was observed in heat capacity data (see footnote \( 8 \)) (typical uncertainty \( \pm0.1 \) K). The anisotropy \( |J_\perp/J| \) is calculated using equation \((3)\). The magnetic properties of a number of other quasi-2D antiferromagnets based on copper–pyrazine coordination complexes can be found in \([26]\).

| Compound                          | \( B_c \) (T) | \( g \)     | \( |J| \) (K) | \( T_N \) (K) | \( |J_\perp/J| \) |
|-----------------------------------|--------------|------------|-------------|-------------|----------------|
| \( \text{[Cu(HF}_2\text{)(pyz)}_2\text{]BF}_4 \) | 18.0         | 2.13 ± 0.01| 6.3         | 1.54        | \( 9 \times 10^{-4} \) |
| \( \text{[Cu(HF}_2\text{)(pyz)}_2\text{]ClO}_4 \text{ } B_\perp \) | 19.1         | 2.30 ± 0.01| 7.3         | 1.94        | \( 2 \times 10^{-3} \) |
| \( \text{[Cu(HF}_2\text{)(pyz)}_2\text{]ClO}_4 \text{ } B_\parallel \) | 20.9         | 2.07 ± 0.01| 7.2         | 1.94        | \( 2 \times 10^{-3} \) |
| \( \text{[Cu(HF}_2\text{)(pyz)}_2\text{]PF}_6 \) | 35.5         | 2.11 ± 0.01| 12.4        | 4.31        | \( 1 \times 10^{-2} \) |
| \( \text{[Cu(HF}_2\text{)(pyz)}_2\text{]SbF}_6 \) | 37.6         | 2.14 ± 0.01| 13.3        | 4.31        | \( 9 \times 10^{-3} \) |
| \( \text{[Cu(HF}_2\text{)(pyz)}_2\text{]AsF}_6 \) | 36.1         | 2.13 ± 0.01| 12.8        | 4.34        | \( 1 \times 10^{-2} \) |
| \( \text{[Cu(pyo)}_2\text{)(pyz)}_2\text{]ClO}_4\text{ } B_\perp \) | 20.8         | 2.30 ± 0.01| 7.9         | \( <2.0 \)  | \( \leq10^{-3} \) |
| \( \text{[Cu(pyo)}_2\text{)(pyz)}_2\text{]ClO}_4\text{ } B_\parallel \) | 22.2         | 2.07 ± 0.01| 7.6         | \( <2.0 \)  | \( \leq10^{-3} \) |
| \( \text{CuF}_2\text{(pyz)}(\text{H}_2\text{O)}_2\text{ } B_\perp \) | 28.8         | 2.42 ± 0.02| 11.6        | 2.54        | \( 3 \times 10^{-4} \) |
| \( \text{CuF}_2\text{(pyz)}(\text{H}_2\text{O)}_2\text{ } B_\parallel \) | 33.1         | 2.09 ± 0.01| 11.5        | 2.54        | \( 4 \times 10^{-4} \) |
| \( \text{Cu(pyz)}_2(\text{ReO}_4)_2 \) | 42.7         | 2.13 ± 0.01| 15.1        | 4.2         | \( 3 \times 10^{-3} \) |
| \( \text{Cu(pyz)}_2(\text{H}_2\text{O)}_2\text{Cr}_2\text{O}_7 \) | 13.3         | 2.13 ± 0.01| 4.7         | \( <1.6 \)  | \( \leq1 \times 10^{-2} \) |

\( ^a \)Although \( \text{CuF}_2\text{(pyz)}(\text{H}_2\text{O)}_2 \) forms linear copper–pyrazine chains, EPR measurements on this compound have shown that the dominant superexchange pathway is through the hydrogen bonds between the water molecules and fluorine ions, and hence almost perpendicular to the chains. The result is a quasi-2D antiferromagnet on a square lattice \([23, 24]\).

\( J \) values in conjunction with Neél temperatures deduced from muon-spin rotation (\( \mu \)SR), it is then possible to gain a good estimate of the exchange anisotropy \( |J_\perp/J| \) for all of the magnets.

Having established these findings using the whole range of compounds, we suggest that in magnets of the form \( \text{[Cu(HF}_2\text{)(pyz)}_2\text{]}X, [18, 19] \) where \( X \) is a non-coordinating counterion, \( J \) and \( J_\perp \) may be influenced by the tilting of the pyz molecule with respect to the 2D planes.

2. Experimental details

The quasi-2D magnets studied in this work are listed in table 1. The samples are produced in single or polycrystalline form via aqueous chemical reaction between the appropriate \( \text{CuX}_2 \) salts and stoichiometric amounts of the ligands; further details are given in \([18, 27]\) and footnote \( 8 \), where structural data derived from x-ray crystallography are also found. For some compounds, it was possible to grow crystals large enough to permit measurements with a single
orientated sample (table 1). In other cases, the materials were either polycrystalline or the crystals too small for accurate orientation; therefore, samples composed of many randomly orientated microcrystals, effectively powders were used. In addition to the characterization described in [18] (see footnote 8) sample g-factors were measured [28] using standard EPR techniques [25, 29].

The pulsed-field magnetization experiments used a 1.5 mm bore, 1.5 mm long, 1500-turn compensated-coil susceptometer, constructed from 50 gauge high-purity copper wire [30, 31]. When a sample is within the coil, the signal is $V \propto (dM/dt)$, where $t$ is the time. Numerical integration is used to evaluate $M$ [30]. The sample is mounted within a 1.3 mm diameter ampoule that can be moved in and out of the coil [30]. Accurate values of $M$ are obtained by subtracting empty coil data from that measured under identical conditions with the sample present.

Fields were provided by the 65 T short-pulse and 100 T multi-shot magnets at NHMFL Los Alamos [32] and a 60 T short-pulse magnet at Oxford. The susceptometer was placed within a $^3$He cryostat providing $T_s$ down to 0.4 K. $B$ was measured by integrating the voltage induced in a ten-turn coil calibrated by observing the de Haas–van Alphen oscillations of the belly orbits of the copper coils of the susceptometer [31].

In cases where sufficient quantities of materials were available, Neél temperatures $T_N$ were measured using the zero-field $\mu$SR technique described in [22] (see also [19, 27]). Muons are a useful probe of magnetic order in anisotropic spin systems, where more conventional measurement techniques often encounter several difficulties. These difficulties stem from the build-up of spin correlations at temperatures above $T_N$, which reduce the amount of entropy available to be ejected upon magnetic ordering (and hence reduce the response of the specific heat at $T_N$), and the quantum renormalization of the magnetic moment due to spin fluctuations (which hampers susceptibility and neutron measurements) [22]. In general, $\mu$SR measurements are unaffected by these issues and have been shown to be sensitive to magnetic order in several anisotropic molecular magnets [19, 22, 27]. Thus, $\mu$SR is vital for accurately determining the transition temperatures of the quasi-2D systems described here.

3. Experimental results

Typical $M(B)$ data are shown in figure 1; all compounds studied (table 1) behaved in a very similar fashion. At higher $T$, $M(B)$ is convex, showing a gradual approach to saturation at high $B$. However, as $T \rightarrow 0$, the $M(B)$ data become concave at lower $B$, with a sharp, ‘elbow’-like transition to a constant saturation magnetization $M_{sat}$ at higher $B$; no further changes in $M$ occur to fields of 85 T with the current materials. We label the field at which the ‘elbow’ occurs $B_c$. As shown in figure 1(b), $B_c$ depends on the crystal’s orientation in the field. However, in such cases, the $M$ data become identical to within experimental accuracy when plotted as $M/M_{sat}$ versus $gB$, where $g$ is the $g$-factor appropriate for that direction of $B$ (figure 1(c) and table 1). This suggests that the $g$-factor anisotropy is responsible for the observed angle dependence of $B_c$.

4. Monte Carlo simulations of magnetization data

The magnetic properties of the materials in table 1 are well described by $S = \frac{1}{2} \text{Cu}^{2+}$ spins on a square lattice. The layers are arranged in a tetragonal structure [18]; coupling between the layers
Figure 1. Pulsed-field magnetization data. (a) Magnetization $M$ of $[\text{Cu(HF}_2\text{)(pyz)}_2]\text{(BF}_4\text{)}$ powder versus field $B$; data for $T = 0.5$, 1.5 and 4.1 K are shown (traces for 0.5 and 1.5 K overlie). (b) Magnetization of $[\text{CuF}_2\text{(pyz)}_2]\text{(H}_2\text{O)}_2$ single crystals with $B$ applied parallel (upper 4 traces) and perpendicular (lower trace, 0.5 K) to the 2D planes. Data for $T = 0.5$, 1.5, 4.1 and 10 K are shown for the $B \parallel$ case. The ‘elbow’ denoting saturation occurs at $B_c = 28.8$ T for $B \parallel$ and $B_c = 33.1$ T for $B \perp$. (c) Normalized $M$ data ($T = 0.5$ K) for $[\text{Cu(HF}_2\text{(pyz)}_2]\text{ClO}_4$ single crystals versus $gB$, where $g$ is the appropriate $g$-factor, for $B$ parallel ($B \parallel$) and perpendicular ($B \perp$) to the 2D planes.

The stochastic series expansion (SSE) method [33]–[35] is a finite-$T$ quantum Monte Carlo (QMC) technique based on importance sampling of the diagonal matrix elements of the density matrix $e^{-\beta H}$, where the inverse $T$ is represented by $\beta$, and $H$ is given by equation (1). Using the ‘operator-loop’ cluster update [34], the autocorrelation time for system sizes considered here (up to $\approx 3 \times 10^4$ spins) is at most a few Monte Carlo sweeps even at the critical $T$ [37] for the onset of magnetic order. Estimates of ground state observables are obtained by using

\[ \mathcal{H} = J \sum_{(i,j)_{xy}} S_i \cdot S_j + J_\perp \sum_{(i,j)_{z}} S_i \cdot S_j - h \sum_i S^z_i, \]
sufficiently large values of $\beta$. We have further found that the statistics of the data obtained can be significantly improved by the use of a tempering scheme [37]–[39]. We use parallel tempering [38, 39], where simulations are run simultaneously on a parallel computer, using a fixed value of $J_\perp$ and different, but closely spaced, values of $h = g\mu_B B$ over the entire range of fields up to saturation. Along with the usual Monte Carlo updates, we attempt to swap the values of fields for SSE configurations (processes) with adjacent values of $h$ at regular intervals (typically after every Monte Carlo step, each time attempting several hundred swaps) according to a scheme that maintains detailed balance in the space of the parallel simulations. This has favorable effects on the simulation dynamics, and reduces the overall statistical errors (at the cost of introducing correlations between the errors, of minor significance here). Implementation of tempering schemes in the context of the SSE method is discussed in [40].

5. Comparisons of model and data

Figure 2(a) shows the predictions of the model for low $T$, and figure 2(b) shows a comparison with typical experimental data. This is made by plotting both model results and experimental data in dimensionless units, $M/M_{\text{sat}}$ and $B/B_c$. As $M_{\text{sat}}$ is known, there is in effect only one variable parameter, $B_c$. The value of $B_c$ is varied until there is a satisfactory overlap of the data
and one of the model curves. The curvature of the data and the presence of the ‘elbow’ place tight constraints on the comparison of data and model allowing $B_c$ and the anisotropy $J_\perp/J$ to be determined accurately. The comparison in figure 2(b) is typical of all of the materials in table 1, with their $M(B)$ data falling between, or closest to, the $J_\perp/J = 0$ or $J_\perp/J = \frac{1}{16}$ numerical curves, indicating a high degree of anisotropy. We shall give further justification for this assertion below.

From equation (1) it is seen that $g \mu_B B_c = 4J + 2J_\perp$, and so for such highly anisotropic magnets the model predicts the ratio $g B_c/|J|$ to take values in the range from $5.95 \text{TK}^{-1}$ ($J_\perp = 0$) to $6.10 \text{TK}^{-1}$ ($J_\perp/J = \frac{1}{16}$). Since the experimental uncertainties involved in the location of $B_c$ are $\sim 1-2\%$, and the errors in $g$ are $\sim 1\%$, no significant loss in accuracy occurs if we employ the mean value,

$$\frac{g B_c}{|J|} \approx 6.03 \text{TK}^{-1},$$

in what follows. To check the model prediction, a fit of the $T$-dependent low-field susceptibility following the method of [41] was used to determine $J$ independently for a selection of compounds (figure 3(a)); the values obtained are compared with $g B_c$ in figure 3(b). As can be seen, the points lie close to the line $g B_c/|J| = 6.2 \pm 0.2 \text{TK}^{-1}$, in good agreement with the predicted value (equation (2)). As noted above, it is possible to determine the value of

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9 Note the definition of $J$ used in [41] differs by a factor of 2 from the one employed in the present paper.

10 An alternative expression that allows fitting of the susceptibility to lower temperatures is found in [26]. For the data in figure 3, the results obtained from both expressions are in excellent agreement.
Bc to a very good accuracy (±1–2%); once the dimensionality of the magnet in question is seen to fall within the limits $J_{\perp}/J \approx 0 - \frac{1}{16}$ using comparisons such as those in figure 2(b), equation (2) almost certainly presents the most accurate method for evaluating $J$. Intralayer exchange energies $J$ derived in this way from measured values of $g$ and $B_c$ are in table 1.

Thus, we have developed a method for determining both $J$ and $T_N$ in anisotropic magnetic systems. In addition, an estimate of the anisotropy $|J_{\perp}/J|$ can be made using the results of quantum Monte Carlo simulations of quasi-2D Heisenberg antiferromagnets [42]. This study found

$$\frac{|J_{\perp}|}{|J|} = \exp \left( 2.43 - 2.30 \times \frac{|J|}{T_N} \right),$$

where both $|J|$ and $T_N$ are measured in K; the resulting values are given in table 1. Note that equation (3) is a rapidly varying function of $|J|/T_N$; small shifts in either parameter result in quite large changes in $|J_{\perp}/J|$. Given the experimental and other errors in $J$ and $T_N$ (≈ a few %), the derived values of $|J_{\perp}/J|$ will probably be within a factor ≈ 2 of the true values. In spite of this caveat, the $|J_{\perp}/J|$ values in table 1 are all ≲ 0.01, in good agreement with the comparison of the model and the magnetization data (e.g. figure 2) that suggested $0 \lesssim |J_{\perp}/J| \lesssim \frac{1}{16}$ for all of the compounds.

6. Systematic trends in the [Cu(HF$_2$)(pyz)$_2$]X family

Having established a reliable method for deriving $J$ and the anisotropy from $M(B)$ and $T_N$, we focus our remaining discussion on the compounds with formula [Cu(HF$_2$)(pyz)$_2$]X, ([18], footnote 8) where X can be ClO$_4$, BF$_4$, PF$_6$, etc (table 1). All of these materials possess very similar extended polymeric structures consisting of 2D, four-fold symmetric [Cu(pyz)$_2$]$^{2+}$ sheets in the ab-planes that are connected along the c-axis by linearly bridging HF$_2$ groups (figure 4) ([18], footnote 8). The Cu–Cu separations are similar along the Cu–(pyz)–Cu and Cu–FHF–Cu (e.g. 0.6852 and 0.6619 nm, respectively, for $X =$ BF$_4$ at room temperature) linkages, so that the structure may be described as pseudo-cubic ([18], footnote 8); the X counterions are placed in the body-center positions within each ‘cube’. The Cu–F and Cu–(pyz) bonds result in the Cu$^{2+}$ d$_{x^2-y^2}$ orbitals lying within the ab-planes, as evidenced by the g-factor anisotropy observed in EPR measurements (table 1); as noted above, the ab-planes also correspond to the 2D planes within which the strong exchange pathways occur.

There is little variation of the in-plane Cu–Cu distance across the [Cu(HF$_2$)(pyz)$_2$]X series ([18], footnote 8); given this similarity, it is at first sight surprising that the in-plane exchange parameters $J$ in table 1 fall into two distinct groups: the compounds with tetrahedral counterions ($X =$ BF$_4$ and ClO$_4$) possess values $J \approx -7$ K and those with octahedral counterions ($X =$ PF$_6$, SbF$_6$ and AsF$_6$) have $J \approx -13$ K. Note also that the compounds with tetrahedral counterions are more anisotropic ($|J_{\perp}/J| \sim 10^{-3}$) than those with octahedral counterions ($|J_{\perp}/J| \sim 10^{-2}$).

We now discuss whether the non-coordinating X counterions can play a direct role as exchange pathways between the Cu$^{2+}$ ions. First of all, the molecules ClO$_4$ and BF$_4$ have radically different electronic orbitals, and yet the in-plane exchange energies for the magnets containing these counterions are very similar (see the first three rows of table 1). Moreover, as mentioned above, the X counterions are not within the 2D Cu$^{2+}$ planes, but at body-center positions within the ‘cubes’ (figure 4). The Cu–X separation is therefore roughly the same for
Figure 4. Experimentally determined ([18], footnote 8) room temperature crystal structures of [Cu(HF$_2$)(pyz)$_2$]X 2D metal–organic magnets. (a) $X = $ SbF$_6$; (b) $X = $ BF$_4$. The Cu ions (red) are bridged by organic pyrazine ligands within the $ab$-planes in which the strong exchange pathways occur. These magnetic layers are separated by HF$_2$ bridging groups. The non-coordinating [SbF$_6$]$^-$ and [BF$_6$]$^-$ counterions inhabit the ‘body-center’ sites of each approximately cubic unit; in all but one of the cubic units in (a) and (b) they have been omitted for clarity. Note that for $X = $ BF$_4$ (b), the planes of the pyrazine molecules are tilted by 31.6$^\circ$ away from being orthogonal to the magnetic layers. However, for $X = $ SbF$_6$ (a), the tilt angle is rather smaller (0$^\circ$ at room temperature). Cu = red, F = green, N = blue, C = gray, H = cyan, Sb = black and B = purple. Hydrogen bonds are shown as dotted lines.

The in-plane and inter-plane directions; if the X counterions played a direct role as exchange pathways, one might expect that the [Cu(HF$_2$)(pyz)$_2$]X compounds would have $|J_\perp/J|$ values that were somewhat larger (i.e. more isotropic) than the values $\sim 10^{-2}$ that are actually observed (see table 1). Therefore, instead of playing a direct role in the exchange, it is more likely that it is an counterion size effect on the crystal structure that is affecting the exchange pathways. The size of the counterion in the direction perpendicular to the planes differs by a factor of approximately 2 at room temperature for the tetrahedral and octahedral counterions (see footnote 8 and figure 4). This leads to a modest change in the respective interlayer Cu–Cu distances, $d_\perp$. For example, there is a $\sim 5\%$ difference between the $X = $ BF$_6$ ($d_\perp \approx 6.62$ Å) and the $X = $ SbF$_6$ ($d_\perp \approx 6.95$ Å) compounds (see footnote 8). This trend in inter-plane distance is opposite to that might be expected given that $J_\perp$ appears to be enhanced in the compounds with octahedral counterions (see table 1), and it certainly cannot by itself account for the large change in the in-plane exchange energy.

The structural difference that may be well responsible for the factor of two change in $J$ is the configuration of the pyz molecules within the Cu–(pyz)–Cu linkages. Figure 4 (upper) shows [Cu(HF$_2$)(pyz)$_2$]SbF$_6$, one of the systems with octahedral counterions; the structures of $X = $ AsF$_6$, PF$_6$ are very similar. At room temperature, geometry of the octahedral counterions allows the pyz ligands to stand up virtually perpendicular to the $ab$ planes (see footnote 8...
and figure 4). By contrast, the planes of the pyz ligands in the compounds with the smaller tetrahedral counterions, \([\text{Cu(HF)}_2(\text{pyz})_2]\text{BF}_4\) (figure 4 (lowest)) and \([\text{Cu(HF)}_2(\text{pyz})_2]\text{ClO}_4\), are not perpendicular to the ab-planes, but are tilted away by 31.6° (X = BF\textsubscript{4}) or 25.8° (X = ClO\textsubscript{4}) in a pattern that preserves the four-fold symmetry of the Cu\textsuperscript{2+} sites (see footnote 8). This suggests that it may be the orientation dependence of the pyz ligand that produces the factor of two differences in \(J\), with the more perpendicularly disposed pyzs (figure 4) presenting a more efficient exchange pathway within the layers.

Although we cannot rule out the possibility of a structural distortion occurring in these compounds as the temperature is reduced, EPR measurements show no evidence for changes in the local symmetry of the magnetic Cu\textsuperscript{2+} ion on cooling to \(T_N\). Therefore, at present it seems unlikely that any such structural reorientation could lead to the observed disparity between the compounds with counterions of different symmetries.

### 7. Summary

Magnetization experiments have been carried out on nine metal–organic Cu-based 2D Heisenberg magnets. These systems exhibit a low-\(T\) magnetization that is concave as a function of field, with a sharp ‘elbow’ transition to a constant saturation value at a critical field \(B_c\). Monte Carlo simulations including interlayer exchange quantitatively reproduce the data; the concavity indicates the effective dimensionality and \(B_c\) is an accurate measure of the in-plane exchange energy \(J\). Taken in conjunction with Neél temperatures derived from \(\mu\text{SR}\), the values of \(J\) may be used to obtain quantitative estimates of the exchange anisotropy, \(|J_\perp/J|\).

We suggest that in metal–organic magnets of the form \([\text{Cu(HF)}_2(\text{pyz})_2]X\), where \(X\) is a non-coordinating counterion molecule, the sizes of \(J\) and \(J_\perp\) may be controlled by the tilting of the pyz molecule with respect to the 2D planes. Thus, it may be possible to use molecular architecture to design magnets with very specific values of \(J\), tailored to a particular desired property.

Another way of looking at these structures is that they are pseudo-perovskite \(A BL_3\), where the \(A\) is the counterion (BF\textsubscript{4}, ClO\textsubscript{4}, etc), Cu is the \(B\) cation and \(L\) are the coordinated bridges, pyz and HF\textsubscript{2}. In light of this, one possible application would be a metal–organic magnet designed to simulate the antiferromagnetic interactions germane to cuprate superconductivity [3], [10]–[14], but with exchange energies small enough to permit manipulation of the magnetic groundstate using standard laboratory fields.

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References

[1] Kastner M A, Birgeneau R J, Shirane G and Endoh Y 1998 Rev. Mod. Phys. 70 897
[2] Schollwöck U, Richter J, Farnell D J J and Bishop R F (ed) 2004 Quantum Magnetism (Berlin: Springer)
[3] Manousakis E 1991 Rev. Mod. Phys. 53 1
[4] Christensen N B et al 2007 Proc. Natl Acad. Sci. USA 104 15264
[5] Vajk O P, Mang P K, Greven M, Gehring P M and Lynn J W 2002 Science 295 1691
[6] Deng D S, Jin X F and Tao T 2002 Phys. Rev. B 65 132406
[7] Beard BB, Cuccoli A, Vaia R and Verrucchi P 2003 Phys. Rev. B 68 104406
[8] Sengupta P, Sandvik A W and Singh R R P 2003 Phys. Rev. B 68 094423
[9] Zhang R and Zhu S Q 2006 Phys. Lett. A 348 110
[10] Schrieffer J R and Brooks J S (ed) 2007 High Temperature Superconductivity Theory and Experiment (Berlin: Springer)
[11] Dai P, Mook H A, Hunt R D and Doğan F 2001 Phys. Rev. B 63 054525
[12] Stock C et al 2005 Phys. Rev. B 71 024522
[13] Julian S R and Norman M 2007 Nature 447 537
[14] Harrison N, McDonald R D and Singleton J 2007 Preprint 0710.1932
[15] Monthoux P, Pines D and Lonzarich G G 2007 Nature 450 1177
[16] Mermin N D and Wagner H 1966 Phys. Rev. Lett. 17 1133
[17] Choi J, Woodward J D, Musfeldt J L, Landee C P and Turnbull M M 2003 Chem. Mater. 15 2797
[18] Manson J L et al 2006 Chem. Commun. 4894
[19] Lancaster T et al 2007 Phys. Rev. B 75 094421
[20] Deumel M, Landee C P, Novaia J J, Robb M A and Turnbull M M 2003 Polyhedron 22 2235
[21] Lancaster T et al 2006 Phys. Rev. B 73 020410
[22] Blundell S J et al 2007 J. Phys. Chem. Solids 68 2039
[23] Manson J L et al 2008 Chem. Mater. submitted
[24] Goddard P A et al 2008 Preprint 0807.1506
[25] Abragam A and Bleaney B 1970 Electron Paramagnetic Resonance of Transition Ions (Oxford: Oxford University Press) p 208
[26] Woodward F M et al 2007 Inorg. Chem. 46 4256
[27] Lancaster T et al 2007 Phys. Rev. Lett. 99 267601
[28] Cox S, McDonald R D, Funk K, Southerland H A, Manson J L and Schlueter J A 2008 in preparation
[29] Poole C P Jr 1982 Electron Spin Resonance: A Comprehensive Treatise on Experimental Techniques (New York: Wiley)
[30] Goddard P A et al 2007 Phys. Rev. B 75 094426
[31] Detwiler J A et al 2000 Phys. Rev. B 61 402
[32] Jaime M, Lacerda A, Takano Y and Boebinger G S 2006 J. Phys.: Conf. Ser. 51 643
[33] Sandvik A W and Kurki-Järvi 1991 Phys. Rev. B 43 5950
[34] Sandvik A W 1997 Phys. Rev. B 56 11678
[35] Sandvik A W 1999 Phys. Rev. B 59 14157
[36] Syljuåsen O F and Sandvik A W 2002 Phys. Rev. E 66 046701
[37] Marinari E 1998 Adv. Comput. Simul. 501 15
[38] Hukushima K, Takayama H and Nemoto K 1996 Int. J. Mod. Phys. C 7 337
[39] Hukushima K and Nemoto K 1996 J. Phys. Soc. Japan 65 1604
[40] Sengupta P, Sandvik A W and Campbell D K 2002 Phys. Rev. B 65 155113
[41] Landee C P, Roberts S A and Willett R D 1978 J. Chem. Phys. 68 4574
[42] Yasuda C et al 2005 Phys. Rev. Lett. 94 217201

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