Spin glassiness and power law scaling in anisotropic triangular spin-1/2 antiferromagnets

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Abstract – We present data on the magnetic properties of two classes of layered spin \( S = 1/2 \) antiferromagnetic quasi-triangular lattice materials: \( \text{Cu}_2(1-x)\text{Zn}_2x(\text{OH})_3\text{NO}_3(0 \leq x \leq 0.65) \) and its long-organic-chain-intercalated derivatives \( \text{Cu}_2(1-x)\text{Zn}_2x(\text{OH})_3(\text{C}_7\text{H}_{15}\text{COO})\cdot m\text{H}_2\text{O}(0 \leq x \leq 0.29) \), where non-magnetic Zn substitutes for Cu isostructurally. It is found that the intercalated compounds, even in a clean system in the absence of dilution, \( x = 0 \), show spin glass behaviour, as evidenced by DC and AC susceptibility, and by time-dependent magnetization measurements. A striking feature is the observation of a sharp crossover between two successive power law regimes in the DC susceptibility above the freezing temperature. In contrast to standard theoretical expectations, these power laws are insensitive to doping. Specific heat data are consistent with a conventional phase transition in the unintercalated compounds, and glassy behaviour in the intercalated compounds.

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Introduction. – The study of both geometric frustration and disorder in quantum magnetism has defined new paradigms of condensed matter for many decades. While frustration plays a major role in compounds like the recently studied “spin liquid” \([1, 2]\) candidate herbertsmithite \([3]\), disorder is thought to be the driving force in systems exhibiting spin glass \([4]\) and quantum Griffiths \([5]\) type behaviour. More controversial is the notion that frustrated interactions alone may also trigger glassy behaviour in clean quantum spin systems. This debate has been further fueled by recent interest in spin-glass and disordered magnets and other random magnets.

Disorder is indicative of the fact that the glassiness may be intrinsic, and due to frustration rather than disorder.

In recent years, chemical doping has proven to be an invaluable tool in accessing an extended phase diagram of transition metal oxides, in particular for detecting otherwise inaccessible transitions. Examples are the high-temperature superconducting cuprates and pnictides, and various heavy-fermion compounds \([12–15]\). These systems display some of the most fascinating and mysterious phase diagrams so far found in electronic phases of matter, and due to the importance of chemical doping in their exploration, unraveling the role of disorder is an ever present complication. Glassiness, as well as power law scaling, are frequent companions of the interesting phases found in these compounds.

In this work, we follow this paradigm by applying Zn doping to study a new family of doped frustrated \( S = 1/2 \) spin systems by building on the nearly triangular geometry of the pure-copper \((x = 0)\) layered compound CHN. The family of compounds, \( \text{Cu}_2(1-x)\text{Zn}_2x(\text{OH})_3(\text{C}_7\text{H}_{15}\text{COO})\cdot m\text{H}_2\text{O} \), consists of long-organic-chain (LOC)–intercalated derivatives of Zn-substituted CHN. Antiferromagnetic layers of Cu spin-1/2 ions forming a distorted triangular lattice are separated by as much as 24 Å as a result of the LOC intercalation (fig. 1). We report a remarkably robust behaviour of the LOC CHN compounds, which manifests itself through two distinct regimes of power law scaling.
in the temperature dependence of the DC susceptibility, separated by a sharp crossover. Moreover, we also identify this behaviour in the undoped parent material. We find that Zn doping enhances this effect, showing it to be a robust feature of the physics of the glassy LOC CHN compounds. Furthermore, we present significant new evidence for the glassiness of both the doped and undoped LOC CHN compounds, where Zn doping randomly removes local moments from the Cu\(^{2+}\) layer, and so dilutes the magnetic lattice and its associated magnetic bonds. The ability to control the Zn concentration sheds new light on the relation between compositional disorder and the glassiness of these systems. In the pure-copper \(x = 0\) case, glassy features had been observed earlier [16].

Structure and preparation. – The structure of the LOC CHN compound is shown in fig. 1. The unit cell contains two inequivalent Cu\(^{2+}\) ions forming distorted triangular layers. The preparation of the undoped samples follows refs. [11] for CHN and [16] for the LOC CHN compounds. The method for preparing the Zn-doped samples has been reported earlier [17]. Powder X-ray diffraction measurements have been carried out [17]. For both LOC CHN and unintercalated diluted CHN samples, Zn was found to replace Cu leading to a series of isostructural doped compounds. The LOC CHN samples are characterized by pronounced (00l) reflections, as is typical for layered structure compounds with large interlayer distances. From this the interlayer distance was obtained to be 24.2 Å, consistent with ref. [16]. This distance was also found to be independent of Zn doping concentration. A detectable ZnO impurity phase was only observed in the \(x = 0.65\) sample.

The number of water molecules in the gallery, \(m\), in the chemical formula Cu\(_{2(1-x)}Zn_{2x}(OH)_{3}(C_7H_{15}COO)\cdot mH_2O\) has not been determined directly, but has been estimated by matching the effective moments of the LOC CHN sample with those of the corresponding CHN samples. If \(m\) takes the integer values 1, 1, 3, and 0, for \(x = 0, 0.13, 0.19, 0.29\) LOC CHN samples, respectively [17], the effective moments of two series of samples agree to within 2%. This method of estimating \(m\) has little effect on our experimental observations except to introduce a small error in the total molecular weight. This change will be reflected in the calculation of effective moments of Cu\(^{2+}\) as noted above.

DC and AC susceptibility. – DC susceptibility data for the diluted CHN system has been reported in ref. [17]. Both the Curie-temperature and the Néel temperature vary with Zn concentration, but are on the order of 10 K in agreement with density functional values for the exchange couplings [18]. The value of the exchange interaction parameter is known to be sensitive to the Cu-OH-Cu bond angle, with both ferromagnetic (FM) and anti-ferromagnetic (AFM) values being possible. In CHN

Fig. 1: (Colour on-line) Structure of the long-organic-chain-intercalated CHN compound. (a) Perspective view of the basal unit. (b) c-axis view of the Cu layer and its planar unit cell. \(a_1 = 3.03\) Å, \(a_2 = 3.17\) Å.
A remarkable feature seen in the log-log plots of fig. 2 is the presence of a sharp crossover between two distinct power law regimes above $T_f$. The first of these regimes corresponds to a temperature window typically between 5 K and 12 K, where $\chi \propto T^{-a}$ with different exponents $a \geq 5$ for $x = 0$ and $a \geq 2$ for $x > 0$. In a second regime at higher temperatures roughly between 12 K and 90 K, $\chi \propto T^{-b}$ with $b \simeq 0.3$ for all samples, below a Curie tail with $\chi \propto T^{-1}$ for $T > 90$ K. This behaviour is slightly more pronounced in the $x > 0$ samples which all have very similar exponents, but is clearly identifiable also in the $x = 0$ sample. Hence the sharp crossover between two different power law regimes as a precursor to the spin glass phase appears to be a robust feature of the physics of the LOC CHN samples. To our knowledge, the finding of power law behaviour that is insensitive to doping has not been reported earlier. We note that FC and ZFC data are indistinguishable in the higher-temperature regime. In the lower-temperature regime, the FC data have been used for the linear fits in fig. 2. However, the ZFC data display power law behaviour with similar exponents even there.

The frequency dependence of the AC susceptibility of the $x = 0$ LOC CHN sample is shown in fig. 3. The real part $\chi'$ was found to be extremely well described by the logarithmic functional form $\chi' = \chi_0 - \text{cln}(\omega)$ at low frequencies $< 10^4$ Hz, a standard behaviour [20] for spin glasses. This is in good agreement with the imaginary part (inset), whose low-frequency limit is a non-zero constant that agrees well with $\pi c/2$ as determined from the real part via Kramers-Kronig relations. These findings provide strong new evidence for spin glass physics in the $x = 0$ LOC CHN sample, even though this system seems to have no apparent structural disorder.

**Time-dependent magnetization.** – The time evolution of the isothermal remanent magnetization $M_{ZFC}(t)$ of the LOC CHN samples has been studied in the following steps. Samples were first cooled in zero field to 2 K (well below the freezing temperature) and then kept in a magnetic field, $H$, for 10 minutes. After switching off the applied field, we measured $M_{ZFC}(t)$ for 5000 seconds. The experiment was repeated in 5 different fields (50 Oe, 500 Oe, 5000 Oe, 10000 Oe and 20000 Oe). The data for the LOC CHN samples with $x = 0$, 0.13, 0.19 and 0.29, whose respective Curie constants were found to be $-94$ K, $-74$ K, $-67$ K and $-64$ K. The susceptibility data are shown in fig. 2. A clear difference between the zero-field–cooled (ZFC) and field-cooled (FC) data below a temperature $T_{ir} \sim 6$–12 K is a first indication of the glassiness of the LOC CHN samples. No similarly large effect has been seen in the diluted CHN samples [17]. Note that the FC susceptibility of the $x = 0$ sample grows by two orders of magnitude between 20 K and 2 K. Such changes have been seen in other spin glasses and electronic glasses in a variety of response functions [19]. It is worth pointing out that in the LOC CHN case, the ZFC/FC difference actually diminishes at finite Zn concentration compared to the undoped parent compound. This may indicate that the glassiness of the system is indeed driven by frustration rather than disorder. Similarly, the freezing temperature $T_f$ as determined by the peak in the ZFC susceptibility is $\sim 8$ K for the $x = 0$ sample, and is $\sim 2$× lower for the Zn-doped samples.

Fig. 2: (Colour on-line). $\ln(\chi)$ vs. $\ln(T)$ for the DC susceptibility of long-organic-chain–intercalated CHN samples. (a) Both field-cooled and zero-field–cooled data are shown with different offsets for different dopings $x$ as indicated. The freezing temperature, $T_f$, and irreversibility temperature, $T_{ir}$, are indicated by arrows. Linear fits identify various temperature regimes where $\chi(T)$ is well described by power laws. In the lower-temperature regimes, FC data was used for the fit. However, the ZFC data is seen to follow similar and in some cases almost identical power laws. (b) Close-up of the $x = 0$ ZFC data. The two power law regimes and their sharp crossover are clearly visible.

the angle is close to the FM-AFM crossover [11] rendering the material weakly anti-ferromagnetic. Interestingly, with increased Zn concentration the Curie constant was found to change sign and become ferromagnetic [17]. There was, however, no FM phase seen at low temperature and a complete analysis of this behaviour would likely need to take into account Dzyaloshinskii-Moriya (DM) interactions, which result from the relatively low symmetry at the Cu site [16].

We will now focus on the LOC CHN samples with $x = 0$, 0.13, 0.19 and 0.29, whose respective Curie constants were found to be $-94$ K, $-74$ K, $-67$ K and $-64$ K. The susceptibility data are shown in fig. 2. A clear difference between the zero-field–cooled (ZFC) and field-cooled (FC) data below a temperature $T_{ir} \sim 6$–12 K is a first indication of the glassiness of the LOC CHN samples. No similarly large effect has been seen in the diluted CHN samples [17]. Note that the FC susceptibility of the $x = 0$ sample grows by two orders of magnitude between 20 K and 2 K. Such changes have been seen in other spin glasses and electronic glasses in a variety of response functions [19]. It is worth pointing out that in the LOC CHN case, the ZFC/FC difference actually diminishes at finite Zn concentration compared to the undoped parent compound. This may indicate that the glassiness of the system is indeed driven by frustration rather than disorder. Similarly, the freezing temperature $T_f$ as determined by the peak in the ZFC susceptibility is $\sim 8$ K for the $x = 0$ sample, and is $\sim 2$× lower for the Zn-doped samples.

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Fig. 3: (Colour on-line). AC susceptibility of $x=0$ sample at $T=10$ K. The real part is fitted to the functional form $\chi'=\chi_0 - c \ln(\omega)$. The linear fit of the imaginary part (inset) approaches $\pi c/2$ at $\omega=0$ to within 2% accuracy.

5000 Oe are shown in fig. 4. The time dependence of $M_{ZFC}(t)$ of the $x=0$ sample is plotted in fig. 4(a), in which we observed a long-time slow non-exponential relaxation. For $t \geq 100$ s, $M_{ZFC}(t)$ can be described by $M_{ZFC}(t) = M_0 - S_R \log(t)$, in which $M_0$ is a constant and the coefficient $S_R$ is the magnetic viscosity. This logarithmic decay law is a characteristic feature of spin-glass–like systems. In order to better compare the relaxation behaviours of other doped samples, a scaled $M_{ZFC}(t)/M(0)$ quantity is plotted in fig. 4(b) instead of the absolute values. At 5000 seconds, their $M_{ZFC}(t)$ values slowly decay to 70–80% of the initial values $M(0)$. Their long-time decay behaviours all follow the logarithmic form with different coefficients $S_R$. The time relaxation of $M_{ZFC}(t)$ under the other 4 fields shows similar behaviour and follows a logarithmic decay law after $t > 100$ s. The initial values $M_{ZFC}(0)$ increase rapidly with field for $H < 5$ kOe and slowly approach their saturation value when $H > 5$ kOe.

**Specific heat.** – Specific heat ($C$) measurements were performed on a Quantum Design PPMS with the relaxation method [21]. The powder samples were compressed into ten 20 mg thin cylindrical disks and attached to a platform by Apiezon N grease. A reference measurement was taken first to obtain the heat capacity of the platform and grease. In the following sample measurement, the reference data was subtracted from the total heat capacity yielding the pure sample $C$. Figure 5 shows the $C$ data. Sharp peaks in the diluted CHN data indicate a large amount of entropy loss during the antiferromagnetic phase transitions. This supports a picture based on the existence of conventional long-range magnetic order in the diluted CHN samples. The peak position of $C/T$ decreases as the Zn doping increases, which is similar to the doping dependence of the DC susceptibility peaks [17]. We should also note that in the temperature range $2$ K $< T < 4$ K, the specific heat has a roughly $T^2$ behaviour. This is also seen up to $T \simeq 20$ K or more in the LOC CHN data, fig. 5(b), as noted for $x=0$ in ref. [16]. We caution that since there are no proper nonmagnetic materials with an analogous lattice structure available, such as those corresponding to $x=1$, the pure magnetic contribution cannot be easily separated. To shed more light on this issue, we compared $C$ in zero field to that in a field of $B=5$ T, where the Zeeman energy is comparable to the magnetic exchange interaction (see above). This has a pronounced effect on the peak structure in the diluted CHN samples, giving further evidence of the magnetic origin of this peak. On the other hand, the effect of the magnetic field on the overall $C$ is very small in the LOC CHN samples. The small difference between $B=0$ and $B=5$ T is barely visible in fig. 5(b), and is found to be of order $0.1$ J/mol K. This small magnetic-field dependence indicates that lattice degrees of freedom dominate $C$.

One may attribute this dominance to the large unit cell of the system, especially for the LOC CHN samples, and
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Fig. 5: (Colour on-line). Specific heat divided by temperature, for diluted CHN (a) and long-organic-chain–intercalated CHN (b) samples, with and without an applied magnetic field of $B = 5T$. Data for different Zn concentration $x$ are mutually offset for clarity.

This is the expected low-$T$ contribution of a spin glass (or structural glass) phase [20,22].

Discussion. – The CHN and LOC CHN family of compounds allows a controlled study of the role of non-magnetic impurities in a layered frustrated spin-$1/2$ compound with glassy behaviour. We have given further evidence for the presence of a spin glass phase in the “clean” ($x = 0$) LOC CHN parent compound, and tracked the observed phenomenology as a function of Zn concentration, $x$. The $x = 0$ limit in the absence of Zn substitution was seen to be the case where the glassy features were most pronounced. This may strengthen earlier claims according to which the spin glass phase is driven by frustration rather than disorder. It is likely that anisotropy introduced by DM interactions also plays a role in the observed behaviour [16,23], especially in view of the weakness of the energy scale associated with exchange interactions. We caution that DM terms are particularly sensitive to the symmetry of the local environment, and thus could be more affected by disorder introduced by the organic chains in the LOC CHN samples. Detailed calculations on the strength of these terms and the disorder necessary to reproduce the observed behaviour are left for future studies.

A remarkable effect was found to emerge at temperatures above $T_f$ in the form of two successive power law regimes in the DC susceptibility with a sharp crossover. This effect was furthermore seen to be robust against Zn doping, becoming rather more pronounced in the $x > 0$ samples. This, together with the small value of the power law exponent seen at higher temperatures, suggest an unconventional nature of the spin glassiness seen in these compounds.

To see this, we note that the occurrence of power laws above a transition into a glassy state is somewhat reminiscent of the picture developed in ref. [24]. There it was argued that a quantum Griffiths phase [5] may be unstable to the formation of a cluster glass phase at low temperatures. Above the transition temperature, the quantum Griffiths behaviour is still expected to be seen, which leads to the observation of power laws in thermodynamic quantities [25]. Specifically, the susceptibility is predicted to be of the form $\chi \propto T^{\alpha - 1}$ with $\alpha > 0$. We note, however, that the value of $\alpha$ in this scenario is not universal, but is expected to depend rather sensitively on doping. This was observed in CePd$_{1-x}$Rh$_x$ [26], where $\alpha$ changes by a factor greater than 4 in response to a change of doping by a few percent. In contrast, the variation of $\alpha = 1 - b$ for the high-$T$ power law regimes seen in fig. 2 is less than 10%. In the quantum-Griffiths–based scenario [25], one also assumes proximity to a quantum critical point, at which $\alpha$ approaches zero. Hence in this scenario, one expects $\alpha$ to be considerably less than 1, whereas $\alpha \approx 0.7$ in our case. Furthermore, the quantum Griffiths scenario can at present only explain the occurrence of a single power law with exponent less than 1, and offers no...
direct explanation for the power law behaviour seen at low temperature. To our knowledge, a crossover between different power laws as seen in the LOC CHN compounds has not been previously observed or predicted, and may well be the hallmark of new physics. The stability of the scaling forms and their insensitivity to doping may be consistent with a picture based on self-generated glassiness [27]. In this case, an intrinsic, frustration-based mechanism may lead to glassy low-temperature physics and overwhelm the doping dependence of the observed power laws. A detailed understanding of this behaviour and the search for possible incarnations in other systems remain an interesting challenge for future work.

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