Anisotropy and Ising-like transition of the $S = 5/2$ two-dimensional Heisenberg antiferromagnet Mn-formate di-Urea

Alessandro Cuccoli, Tommaso Roscilde, Valerio Tognetti, Ruggero Vaia and Paola Verrucchi

1 Dipartimento di Fisica dell’Università di Firenze, Via G. Sansone 1, I-50019 Sesto Fiorentino (FI), Italy
2 Istituto Nazionale per la Fisica della Materia (INFM), Unità di Ricerca di Firenze, Via G. Sansone 1, I-50019 Sesto Fiorentino (FI), Italy
3 Dipartimento di Fisica "A. Volta" dell’Università di Pavia, via A. Bassi 6, I-27100 Pavia
4 Istituto Nazionale per la Fisica della Materia (INFM), Unità di Ricerca di Pavia, via A. Bassi 6, I-27100 Pavia
5 Istituto di Fisica Applicata ‘N. Carrara’ del Consiglio Nazionale delle Ricerche, via Panciatichi 56/30, I-50127 Firenze, Italy

(PACS numbers: 75.10.Jm, 05.30.-d, 75.40.-s, 75.40.Cx)

(Dated: January 8, 2022)

Recently reported measurements of specific heat on the compound Mn-formate di-Urea (Mn-f-2U) by Takeda et al. [Phys. Rev. B 63, 024425 (2001)] are considered. As a model to describe the overall thermodynamic behavior of such compound, the easy-axis two-dimensional Heisenberg antiferromagnet is proposed and studied by means of the pure quantum self-consistent harmonic approximation (PQSCHA). In particular it is shown that, when the temperature decreases, the compound exhibits a crossover from 2D-Heisenberg to 2D-Ising behavior, followed by a 2D-Ising-like phase transition, whose location allows to get a reliable estimate of the easy-axis anisotropy driving the transition itself. Below the critical temperature $T_n = 3.77$ K, the specific heat is well described by the two-dimensional easy-axis model down to a temperature $T' = 1.47$ K where a $T^3$-law sets in, possibly marking a low-temperature crossover of magnetic fluctuations from two to three dimensions.

The quantum Heisenberg antiferromagnet (QHAF) on the square lattice is one of the most widely investigated magnetic models because of both its fundamental theoretical properties and the existence of many real compounds whose magnetic behavior is ruled by a spin-spin interaction properly described by the 2D QHAF Hamiltonian. Due to their layered structures, such compounds have an intralayer exchange integral $J$ which is much larger than the interlayer one, $J'$. This ensures a 2D thermodynamic behavior to persist down to a certain crossover temperature which could be naively estimated of the order of $J' S^2$. However, most of the above mentioned compounds display a phase transition towards an ordered phase at a critical temperature of the order of $J S^2$.

If one assumes a fully isotropic intralayer interaction, which cannot induce any finite temperature transition by itself, this experimental finding may be explained by noticing that strong correlations between spins on a single layer act as an effective amplifier of the interlayer interaction, in that the coupling between neighboring spins on different layers drags in a similar coupling the surrounding spins within a distance of the order of the 2D magnetic correlation length $\xi$. However, most of the experimentally observed phase transitions do also display features which suggest a persistent 2D behavior, and are not compatible with the above sketched mechanism. On the other hand, such experimental observations may be explained by allowing the intralayer interaction to be anisotropic; the existence of some anisotropic coupling may hence be invoked, and a more detailed analysis developed.

In this paper we consider the quasi-two-dimensional real compound Mn(HCOO)$_2$·2(NH$_2$)$_2$CO (Mn-formate di-Urea, or Mn-f-2U), which is a remarkable realization of a $S = 5/2$ 2D QHAF in a wide temperature region. From specific-heat and susceptibility measurements, the intralayer spin-spin coupling $J$ turns out to be $J = 0.68 \pm 0.04$ K, while $J'$ is orders of magnitude lower. Characteristic features of a phase-transition, such as a sharp peak in the specific heat, are also observed at $T_n = 3.77 \pm 0.02$ K and suggested the existence of an easy-axis anisotropy in the intralayer spin-spin coupling. By proton NMR measurements it has been established in Ref. [2] that the interlayer coupling is much smaller than the anisotropy, which has been estimated to be of the order of $10^{-2} J$.

We hence propose, as a model for the thermodynamics of Mn-f-2U, the $S = 5/2$ QHAF on the square lattice with easy-axis exchange anisotropy (EA-QHAF), whose Hamiltonian reads

$$\hat{\mathcal{H}} = \frac{J}{2} \sum_{i,d} \left[ \mu \left( \hat{S}_i^x \hat{S}_{i+d}^x + \hat{S}_i^y \hat{S}_{i+d}^y + \hat{S}_i^z \hat{S}_{i+d}^z \right) \right],$$

where $\hat{S}_i^\alpha$ runs over the sites of a square lattice, $d$ connects each site to its four nearest neighbors, $J > 0$ is the antiferromagnetic exchange integral and $\mu \in [0,1]$ is the easy-axis anisotropy parameter. The spin operators $\hat{S}_i^\alpha (\alpha = x, y, z)$ are such that $|S|^2 = S(S+1)$ and obey $[\hat{S}_i^\alpha, \hat{S}_j^\beta] = i \varepsilon_{\alpha\beta\gamma} \hat{S}_i^\gamma$. Classical and quantum Monte Carlo simulations predict such model to display a 2D-Ising phase transition at a finite temperature $T_n(\mu)$, which continuously decreases as $\mu$ increases, finally vanishing for $\mu \to 1$, i.e., in
the isotropic model. The picture in the case of Mn-f-2U is hence that its 2D-Ising transition at $T_i$ immediately triggers the observed phase transition to 3D long-range order: therefore, we assume $T_i = T_c$.

We use the pure-quantum self-consistent harmonic approximation (PQSCHA), a semiclassical method which reduces the expressions of quantum statistical averages to effective classical-like ones, where temperature- and spin-dependent renormalization parameters appear; the thermodynamics of the effective model can then be studied by means of classical techniques, like classical Monte Carlo simulations. Besides a uniform indifferent term that does not affect the evaluation of statistical averages, the PQSCHA effective Hamiltonian for the EA-QHAF reads

$$H_{\text{eff}} = -\frac{J_{\text{eff}}}{2} \sum_{i,d} \left[ \mu_{\text{eff}} (s_i^x s_{i+d}^x + s_i^y s_{i+d}^y + s_i^z s_{i+d}^z) \right],$$

(2)

where $\tilde{S} = S + 1/2$ and $s_i = (s_i^x, s_i^y, s_i^z)$ are classical unit vectors, $J_{\text{eff}}(t, S, \mu) < J$ and $\mu_{\text{eff}}(t, S, \mu) > \mu$ are the renormalized exchange and anisotropy of the effective classical model, respectively. Hereafter the dimensionless temperature $t = T/J\tilde{S}^2$ is used.

This method was applied to the EA-QHAF, and, in particular, to the study of the $\mu$- and $S$-dependence of the Ising critical temperature, which is shown in the phase diagram $t_i(S, \mu)$ reported in Ref. 9. Using that phase diagram, the anisotropy value corresponding to the experimental critical temperature of Mn-f-2U, $t_i = 0.616 \pm 0.039$, is $\mu = 0.981^{+0.014}_{-0.029}$, the large error being due to the experimental uncertainty on $J$. This anisotropy estimate is close to that of the compound Rb$_2$MnF$_4$, a $S = 5/2$ EA-QHAF we have extensively investigated in Ref. 10, namely $\mu = 0.9942$. Moreover, performing a new set of classical MC simulations with a slightly different value of $\mu$, more fit to the case of Mn-f-2U, is, at present, too large an effort compared to the expected benefits. As a matter of fact, due to the poor knowledge of $J$, any choice of the value of $\mu$ in the interval estimated above is affected by a high degree of arbitrariness. We will hence hereafter use the already known PQSCHA curves for $\mu = 0.9942$, owing to the proximity between the two anisotropies (i.e., $\mu = 0.981^{+0.014}_{-0.029}$ estimated for Mn-f-2U from our phase diagram, and $\mu = 0.9942$ corresponding to our previous theoretical data), we expect to be able to single out the characteristic features of the experimental data by comparison with the theoretical curves.

Focusing our attention on recent measurements of the magnetic specific heat of Mn-f-2U, we make a twofold comparison of such data with our predictions for the EA-QHAF. The first comparison, shown in Fig. 1, is made between the measured specific heat of Mn-f-2U and the theoretical one with $\mu = 0.9942$ as a function of the dimensionless temperature. Besides these data, two PQSCHA curves for the $S = 5/2$ isotropic model are also reported: the dashed one is obtained within the same approximation level as for the anisotropic model, while the dotted one is obtained by an improved version of the PQSCHA scheme that was only applied to the isotropic case; the latter was already compared to the experimental data by Takeda et al., so it is included in order to avoid mistakes. Both the theoretical specific heat for the EA-QHAF with $\mu = 0.9942$ and the measured specific heat of Mn-f-2U are seen to behave as that of the isotropic QHAF for temperatures well above $t_i$. The agreement with the isotropic behavior, however, gets worse once the anisotropy starts to drive the anisotropic systems towards the Ising critical regime. The temperature where the anisotropic (solid) curve deviates from the isotropic (dashed) one to form the Ising spike marks a crossover between the Heisenberg and the Ising regime. This crossover, the position of the peak, and the whole behavior below the critical temperature depend on the anisotropy value $\mu$. We stress that if we had calculated the PQSCHA curve for the value $\mu = 0.981$ estimated from the PQSCHA phase diagram, the position of the theoretical peak would coincide with that of the experimental one.

In order to emphasize the common features of the theoretical and the experimental curves in the Ising regime we scale their abscissa $t$ with the actual critical temperatures, i.e., $t_i \equiv T_i/J\tilde{S}^2 = 0.616$ for the experimental data, and $t_i = 0.575$ for the theoretical ones, making the peaks match as shown in Fig. 1. In this way, remarkable agreement between experiment and theory shows up not only for the shape of the transition peak but also for the whole temperature region between $t/t_i = 1$, and $t^*/t_i \approx 0.42$, where the experimental data for the compound Mn-f-2U depart from the PQSCHA curve.

These results show that the compound Mn-f-2U, besides behaving as a 2D EA-QHAF above and in the critical region, displays such behavior in its specific heat also below $t_i$, down to a much lower temperature $t^* \approx 0.24.$
This suggests that below $t_1$, even though the weak interlayer coupling drives the system into a 3D ordered phase, magnetic fluctuations, upon which the specific heat directly depends, remain confined within the layers, being those between different layers incoherent. The 2D picture of the ordered phase eventually breaks down at $t = t^*$. Below this point the experimental data for Mn-f-2U are much better described by a simple $t^3$-law; such law characterizes the low-$t$ region of a 3D quantum antiferromagnet, with the main contribution arising from linear excitations. The temperature $t^*$ could thus be interpreted as marking the dimensional crossover from 2D to 3D behavior, corresponding to the onset of coherence in the magnetic excitations propagating perpendicularly to the layers. However, at this stage, the microscopic mechanism responsible for the observed low-$t$ behavior cannot be firmly identified; nonetheless, the above picture seems to be the simplest one that accounts for the experimentally observed behavior.

In conclusion, we have compared the theoretical findings based on the PQSCHA for the 2D EA-QHAF with recent specific heat data on Mn-f-2U. The comparison reveals the existence of a crossover from a high-temperature 2D-Heisenberg regime to a critical 2D-Ising regime that triggers the phase transition at $T_\text{c} = 3.77$ K observed in Ref. 2. In the ordered phase, the specific heat still behaves as that of a 2D EA-QHAF down to the temperature $T^* = J S^2 t^* \approx 1.47$ K, where 3D behavior sets in. The success of the EA-QHAF model in describing the specific heat of Mn-f-2U in a wide temperature range makes trustworthy our prediction for the value of the anisotropy parameter, $\mu = 0.981$, as obtained above by the sole knowledge of $t_1 = T_\text{c}/(JS^2)$. The above value of $\mu$ implies the anisotropy to be about 1.9% of the exchange energy. Accounting for the large uncertainty upon the estimated $J$, however, the actual anisotropy could range from 0.6% to 4.5%. Anyhow, the above estimate of the anisotropy strength is compatible with the one made by Kubo et al. in Ref. 3. Experiments on Mn-f-2U aimed at a more precise determination of both $J$ and $\mu$, as well as at the characterization of magnetic excitations, such as inelastic neutron scattering ones, come now to be highly desirable.

Acknowledgments

We thank prof. K. Takeda for sending us the experimental data on Mn-f-2U, published in Ref. 4. This work has been partially supported by the COFIN2000-MURST fund, and by the CRUI within the VIGONI programme.

---

1. J. Villain and J.M. Loveluck, J. de Phys. (Lettres) 38, L77 (1977).
2. K. Takeda, H. Deguchi, T. Hoshiko, and K. Yamagata, J. Phys. Soc. Jap. 58, 3489 (1989).
3. K. Takeda, O. Fujita, M. Hitaka, M. Mito, T. Kawae, Y. Higuchi, H. Deguchi, Y. Muraoka, K. Zenmyo, H. Kubo, M. Tokita, and K. Yamagata, J. Phys. Soc. Jap. 69, 3696 (2000).
4. K. Takeda, M. Mito, K. Nakajima, K. Kakurai, and K. Yamagata, Phys. Rev. B 63, 024425 (2001).
5. H. Kubo, K. Zenmyo, M. Tokita, M. Matsumura, K. Takeda, T. Oohashi, and K. Yamagata, J. Phys. Soc. Jap. 69, 2669 (2000).
6. J. D. Patterson and G. L. Jones, Phys. Rev. B 3, 131 (1971); K. Binder and L. P. Landau, Phys. Rev. B 13, 1140 (1976); P. A. Serena, N. García, and A. Levanyuk, Phys. Rev. B 47, 5027 (1993); M. E. Gourvía, G.M. Wysin, S.A. Leonel, A.S.T. Fires, T. Kamppeter, and F.G. Mertens, Phys. Rev. B 59, 6229 (1999).
7. H.-Q. Ding, J. Phys.: Condens. Matt. 2, 7979 (1990); S.S. Aplesin, J. Phys.: Condens. Matt. 10, 10061 (1998), phys. stat. sol. (b) 207, 491 (1998); A. Cuccoli, T. Roscilde, V. Tognetti, P. Verrucchi, and R. Vaia, cond-mat/0209316.
8. A. Cuccoli, V. Tognetti, P. Verrucchi, and R. Vaia, Phys. Rev. B 46, 11601 (1992); A. Cuccoli, R. Giachetti, V. Tognetti, P. Verrucchi, and R. Vaia, J. Phys.: Condens. Matter 7, 7891 (1995).
9. A. Cuccoli, T. Roscilde, V. Tognetti, P. Verrucchi, and R. Vaia, Eur. Phys. J. B 55 (2001).
10. A. Cuccoli, T. Roscilde, V. Tognetti, P. Verrucchi, and R. Vaia, Phys. Rev. B 62, 3771 (2000).
11. A. Cuccoli, V. Tognetti, P. Verrucchi, and R. Vaia, Phys. Rev. B 56, 14456 (1997).