

An ESR study of the diamagnetically doped $S=1/2$ square Heisenberg antiferromagnets $\text{Cu}_{1-x}\text{Mg}_x(\text{HCO}_2)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Cu}_{1-x}\text{Zn}_x(\text{HCO}_2)_2 \cdot 4\text{H}_2\text{O}$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 6217

(<http://iopscience.iop.org/0953-8984/4/29/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 12:22

Please note that [terms and conditions apply](#).

An ESR study of the diamagnetically doped $S = \frac{1}{2}$ square Heisenberg antiferromagnets $\text{Cu}_{1-x}\text{Mg}_x(\text{HCO}_2)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Cu}_{1-x}\text{Zn}_x(\text{HCO}_2)_2 \cdot 4\text{H}_2\text{O}$

S J Clarke and A Harrison

Inorganic Chemistry Laboratory, Oxford University, South Parks Rd., Oxford OX1 3QR, UK

Received 19 February 1992

Abstract. The two-dimensional (2D) $S = \frac{1}{2}$ Heisenberg antiferromagnet copper (II) formate tetrahydrate ($\text{Cu}(\text{HCO}_2)_2 \cdot 4\text{H}_2\text{O}$) has been doped with the diamagnetic ions Mg^{2+} and Zn^{2+} up to levels of 15 at.%. The temperature dependence of the electron spin resonance (ESR) signal provides a way of accurately determining the differences in the Néel temperatures, $T_N(x)$, of samples with different dopant concentrations, x . There is a linear decrease of T_N with increasing dopant concentration: $T_N(x) = (1 - \alpha x)T_N(0)$ where the constant α is 3.4 ± 0.1 and $T_N(0)$ is the Néel temperature of the undoped material. This behaviour is compared with that of La_2CuO_4 and other 2D systems. The width of the ESR signal at a particular temperature is also found to decrease with increasing dopant concentration. These features, together with the variation of linewidth with temperature characteristic of 2D systems, are discussed in the light of the interactions between the magnetic ions.

1. Introduction

The class of two-dimensional Heisenberg antiferromagnets (2DHAF) with $S = \frac{1}{2}$ on a square lattice with the magnetic Hamiltonian

$$\mathcal{H} = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \quad (1)$$

where J is the nearest-neighbour intra-plane exchange constant, has not been well characterized because few model materials have been discovered to date. The rare earth cuprate superconductors [1–3] appear to belong to this class of magnet but they are not ideal models because they are difficult to prepare as large, homogeneous single crystals. Further, the in-plane exchange constant of around 1200 K renders the zone boundary inaccessible to most inelastic neutron spectrometers, a notable exception being the High Energy Transfer spectrometer at ISIS [4].

The search for new materials to model the 2DHAF led us to copper (II) formate tetrahydrate, $\text{Cu}(\text{HCO}_2)_2 \cdot 4\text{H}_2\text{O}$ (CFTH) which had been the subject of numerous investigations [5–10] before its relation to the high- T_c materials was pointed out [11, 12]. The structure of CFTH is shown in figure 1. The unit cell is monoclinic and the space group is $P2_1/a$ at room temperature with the lattice parameters $a = 8.15 \text{ \AA}$,

$b = 8.18 \text{ \AA}$, $c = 6.354 \text{ \AA}$ and $\beta = 101.1^\circ$. The copper ions, which lie in the ab plane, are each linked to four others by formate groups. The copper formate layers are separated by hydrogen bonded water molecules. At 246 K there is an antiferroelectric phase transition due to ordering among the water molecules and this leads to a doubling of the unit cell along the c -axis [13, 14]. J is approximately 80 K and the inter-plane exchange constant, J' , is estimated to be less than $10^{-3}J$. At $T_N \approx 16.5 \text{ K}$ there is a phase transition to 3D antiferromagnetic order driven by J' [5]. In the ordered state the magnetic moments form a 4-sublattice array. The magnetic unit cell has the same dimensions as the crystallographic unit cell [15].

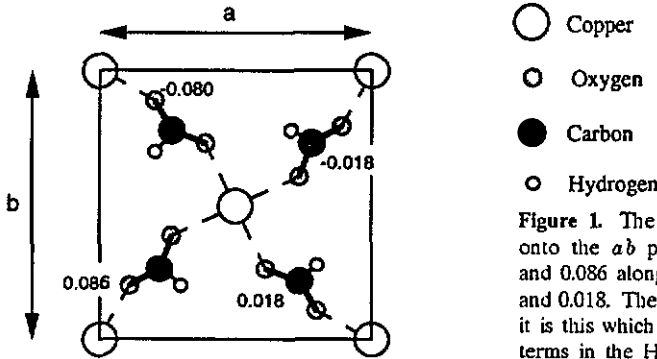


Figure 1. The crystal structure of CFTH projected onto the ab plane. Oxygen atoms are at -0.080 and 0.086 along c and carbon atoms are at -0.018 and 0.018 . The planes are non-centrosymmetric and it is this which can lead to antisymmetric exchange terms in the Hamiltonian.

We have already performed neutron scattering measurements on the fully deuterated form of CFTH [11, 12]. Elastic neutron scattering measurements below T_N [11] produced a value of the critical exponent for the order parameter of 0.23 ± 0.1 which is exhibited by a large number of other 2D systems [7, 16–18]. The exponent was found to change to 0.32 ± 0.1 close to T_N . Similar results were obtained by NMR measurements [7]. Quasielastic neutron scattering between T_N and $2T_N$ [11] produced a value for J of 84 K and showed that, like in La_2CuO_4 [19], the behaviour of the 2D fluctuations in the paramagnetic phase could be treated by the theory of Chakravarty *et al* [3, 20, 21]. Inelastic neutron scattering measurements [12] were used to study the spin-wave spectrum close to the zone centre at $T_N/4$. These confirmed the 2D Heisenberg nature of the spin correlations and produced a value for J of 95 K.

There has been speculation that there may be novel behaviour associated with diamagnetic doping of the 2DHAF with $S = \frac{1}{2}$ due to the proposed quantum nature of the ground state. Initial results on La_2CuO_4 doped with Zn^{2+} [22] suggested that the rate at which T_N was depressed on doping was about nine times that of classical 2DHAFs at low dopant concentrations. However, more recent magnetic susceptibility measurements indicate that the rate of depression of T_N is about the same as that of classical magnets [23] and that the earlier results arose from the combined effects of diamagnetic doping and additional oxygen incorporated into the structure during preparation. The present work was carried out to compare the behaviour of CFTH with that of classical 2DHAFs. Mg^{2+} and Zn^{2+} are non-magnetic divalent ions of similar size to Cu^{2+} . Mg^{2+} favours an octahedral coordination when bound to O^{2-} and was initially chosen as the dopant ion because it was thought that it would not disrupt the crystal structure as much as Zn^{2+} which prefers to adopt a tetrahedral coordination with O^{2-} .

2. Experiment and results

Samples were prepared by dissolving mixtures of basic copper (II) carbonate and magnesium (II) or zinc (II) carbonate in an aqueous solution of 10% formic acid. Single crystals with sizes ranging from 1 to 1000 mm³ were grown by slowly evaporating solutions at room temperature.

The proportion of Mg²⁺ in solution which could be incorporated into crystals of Cu_{1-x}Mg_x(HCO₂)₂·4H₂O (CFTH:Mg²⁺) was small and a dopant level of only 2.3 at.% could be obtained by growing crystals at room temperature from a solution containing 30 at.% Mg²⁺. If the solution contained a higher concentration of Mg²⁺, a multiphase precipitate was produced which was believed to be a mixture of CFTH:Mg²⁺ and magnesium (II) formate. It was possible to grow crystals containing up to 3.3% Mg²⁺ by elevating the growing temperature to 34.5°C. However, these were extensively twinned and did not produce good quality electron spin resonance (ESR) spectra.

It was found that CFTH could be doped with much higher concentrations of Zn²⁺. Crystals of Cu_{1-x}Zn_x(HCO₂)₂·4H₂O (CFTH:Zn²⁺) containing up to 15% Zn²⁺ could be grown from solutions containing up to 30% Zn²⁺. The characteristic crystal morphology of CFTH [24] was unchanged on doping with Mg²⁺ or Zn²⁺ indicating that the diamagnetic ions are incorporated into the structure without distorting it appreciably. However, the samples containing about 15% Zn²⁺ contained visible defects. Single crystals were prepared containing 0.9 and 2.3% Mg²⁺ and 2.25, 4.32, 5.91, 10.7, 12.8, 14.1, 14.5 and 15.3% Zn²⁺. It has not yet proved possible to increase further the concentration of Zn²⁺ in the crystals. The relative concentrations of Cu²⁺ and Mg²⁺ or Zn²⁺ were determined spectrophotometrically using about 10 mg of the sample from which the crystal used in the ESR measurements had been cut. The total metal ion content was compatible with that expected for a compound with the stoichiometry of CFTH.

ESR was chosen as the initial probe of the magnetic properties of the doped material because it is a sensitive technique from which a large amount of information can be obtained and because there have already been extensive ESR measurements performed on CFTH itself [8–10, 25] and on related 2D systems [26, 27].

ESR measurements on each sample were carried out using a 9.3 GHz Varian E-Line Century Series EPR Spectrometer at the Inorganic Chemistry Laboratory in Oxford. A single crystal with approximate dimensions 1×1×2 mm was cut from a larger crystal using a scalpel and mounted on a piece of Teflon and this was sealed inside a Spectrasil tube in order to prevent dehydration of the sample. The sample was oriented by eye using the crystal morphology so that the *ab* plane, containing the Cu²⁺ ions coupled by *J*, was vertical. This could be achieved to within about 3°. The magnetic component of the microwave field, *B*, was also vertical and the applied magnetic field, *H*, was horizontal.

Two experiments were performed. In the first, the sample was rotated in 10° intervals through an angle θ about a vertical axis and the spectrum was recorded at room temperature as a function of θ . $\theta=0$ was defined to be the orientation in which *H* was perpendicular to the Cu²⁺ planes. The spectrum is broadened by spin-spin interactions between pairs of Cu²⁺ ions. For the undoped material, the width is 250 G at room temperature when $\theta=0$. The spectra were fitted to Lorentzian curves. The linewidth decreased by about 15% as θ was changed from 0 to $\pi/2$. The *g*-value, determined by calibration of the instrument using diphenylpicrylhydrazyl (DPPH), varies from 2.36 at $\theta=0$ to 2.12 at $\theta = \pi/2$ and exhibits a dependence on

θ of the form $g = A + B \cos 2\theta$; this is illustrated in figure 2. This behaviour was qualitatively and quantitatively the same as that observed by Shimada *et al* [25] using the same spectrometer configuration. The variation in g -value can be understood from a knowledge of the relative energies of the d-orbitals for a Jahn–Teller distorted octahedral symmetry. The unpaired electron is in the highest energy orbital which has $d_{x^2-y^2}$ character. Rotation of this half-filled orbital about the z axis leads to an angular momentum contribution along the z direction which in this case is perpendicular to the plane of Cu^{2+} ions. This is expected to increase the value of g_z relative to g_{xy} and this is the observed behaviour. Unfortunately, the configuration of the spectrometer confined the microwave magnetic field to be in a fixed orientation relative to the metal ion planes. It was not possible to rotate the crystal accurately or continuously, so this field moved from being in the planes to being perpendicular to them.

In the second series of experiments, the samples were oriented with the applied magnetic field perpendicular to the planes of metal ions. The samples were cooled using an Oxford Instruments ^4He flow cryostat and the temperature was measured using an Oxford Instruments Intelligent Temperature Controller. Liquid nitrogen was used as the single fixed reference point for the temperature. Because of the duration of the series of experiments, the value of this fixed point was found to change by up to 0.4 K due to the effects of atmospheric pressure which fluctuated between 998 and 1035 mb; the measured temperature was corrected for this.

The top face of each sample was mounted in the same position in the tube to within 0.1 mm and the tube was mounted in the same position inside the cryostat to within 0.2 mm. This was in order to eliminate systematic errors in measuring the temperatures of different samples due to them being located in different positions in the temperature gradient within the cryostat. The samples were all of the same volume (about 2 mm^3) to within a factor of two. This was not only to ensure that each one reached thermal equilibrium over the same time-scale, but to ensure that there was no difference in the instrumental broadening of the signals of different samples. Such broadening was observed by Seehra and Castner (SC) [9, 10] who used samples varying in size from 0.4 mm^3 to 10 mm^3 and arises from magnetic losses in the sample when it is large compared with the microwave cavity. Comparison of the spectra of samples of volume 2 mm^3 and 12 mm^3 showed no difference in the linewidths at all temperatures. This indicates that our cavity is sufficiently large for the sample size effect to be small for the samples used. However, we did notice that when the sample was large and the temperature was close to T_N there was appreciable peak asymmetry due to microwave absorption by the sample.

Sample equilibration was found to be rapid because of the good thermal conductivity of helium gas. A typical equilibration time of seven minutes was allowed while the temperature was changed by about 2 K in the 25 K region. However the temporal dependence of the sample signal during the change would suggest that thermal equilibration had occurred over about two or three minutes.

The resonance occurs at $g = 2.36$ in this configuration and was recorded at a number of temperatures from 3–4 K below T_N to room temperature. Very close to T_N , where the resonance is weak, a second peak was observed at a g -value of 2.16. This peak increased greatly in intensity when the sample was allowed to partially dehydrate on exposure to the atmosphere for three hours at room temperature. The peak was thus ascribed to the presence of small quantities of dehydrated material on the surface of the sample. This 'impurity' peak was also observed by SC [9] who

also ascribed it to dehydrated material. The signal at each temperature was fitted to a Lorentzian curve. If the impurity peak was intense it was found to partially obscure the signal close to T_N , although in all cases at least half of the signal could be fitted. The Lorentzian function was found to describe the lineshape accurately between 300 and 25 K but less well at lower temperatures. The function was used throughout however, because it was found to give an accurate measure of the full width at half maximum (FWHM) at all temperatures. The error in the measurement of the linewidth is typically 1–3 G. For the pure material, the linewidth decreases linearly from 250 G at room temperature to around 100 G at 70 K as shown in figure 3. From 70 to 30 K, the decrease is still linear, but faster than before. The linewidth reaches a minimum of around 50 G at about 25 K and then increases steeply. The divergence is approximately linear and very rapid close to T_N . It may be that the change in gradient around 70 K is related to the broad susceptibility maximum noted by Seehra [29] and manifested in these experiments as a broad maximum in the signal intensity. The change in gradient was also observed by SC [9] at 9 GHz and they first offered this explanation for its origin.

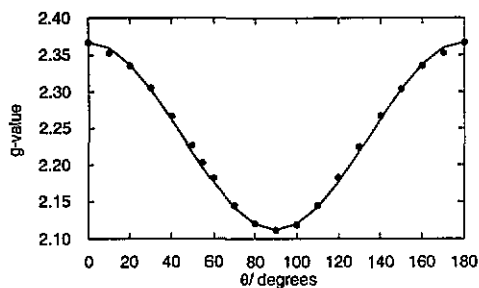


Figure 2. The angular dependence of the g -value of CFTH. θ is the angle between the applied magnetic field and the perpendicular to the magnetic planes.

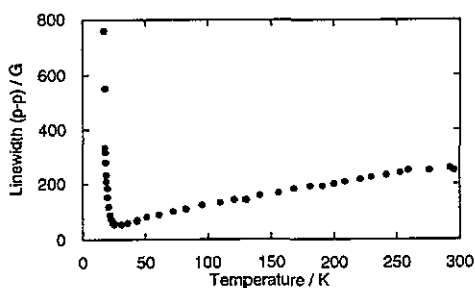


Figure 3. The dependence of the ESR linewidth of CFTH on temperature.

As the concentration of the diamagnetic dopant ion increased, there were changes in the behaviour of the linewidth as a function of temperature. Firstly, the temperature at which the divergence occurred decreased linearly with increasing dopant concentration. Since the divergence is linear and very rapid close to T_N , this provides a way of accurately determining the differences in T_N of different samples. Secondly, the resonances of doped samples were found to be narrower than those of the pure material at all temperatures. The Zn^{2+} -doped samples containing about 15% Zn^{2+} possess resonances which reach minima of about 36 G. The temperatures at which the minima occur also depend on dopant concentration due to the differences in T_N .

The intensity of the resonances increases linearly to a broad maximum before decreasing sharply as T_N is approached. This is shown in figure 4 for CFTH. The position of the resonance with the crystal in a fixed orientation is independent of temperature between room temperature and just above T_N at which point it increases sharply as shown in figure 4(b). The increase of g -value corresponds to an ordering field of about 300 G.

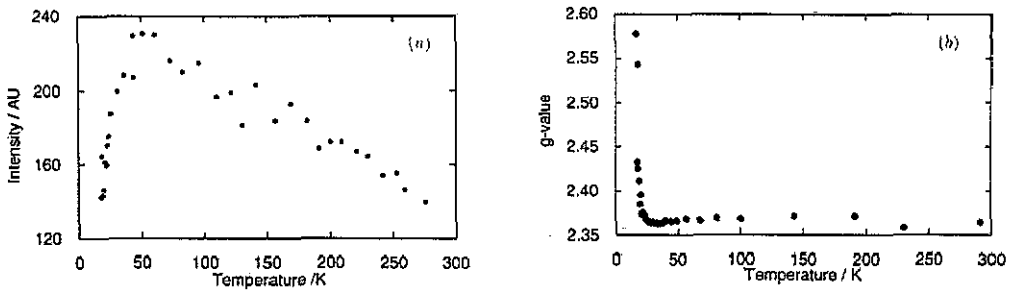


Figure 4. The dependence of (a) the ESR signal intensity and (b) the g -value with the applied field perpendicular to the planes of CFTH on temperature.

3. Discussion

3.1. Dependence of the linewidth on temperature

Consider the effects leading to ESR line broadening in two-dimensional systems and the effects of temperature on these.

Anisotropic interactions between spins have the effect of broadening the resonance into a Gaussian shape with a width in frequency units of $\Delta\omega$ defined as M_2 , the second moment of the lineshape. If the isotropic superexchange interaction of strength J is large then this causes the frequency ω_e of the magnetic fluctuations to be larger than M_2 and causes the field due to the spin-spin interactions to be averaged to zero in a time $1/\omega_e$ which is less than the relaxation time $1/\Delta\omega$. This leads to exchange narrowing of the resonance.

The major contributions to the broadening arise from the dipolar interaction and from antisymmetric exchange if it is allowed by symmetry. Additional contributions from symmetric anisotropic exchange and crystal field fine structure are usually small enough to be neglected. Richards and Salamon [28] showed that when the major contribution to line-broadening in a 2D system arises from the dipolar interaction, the relaxation process is dominated by long-wavelength phonon modes and this leads to a linear dependence of the linewidth on temperature, T , when $T \gg T_N$. This is the situation in K_2MnF_4 in which the planes are centrosymmetric and there is no possibility of an antisymmetric exchange interaction. In CFTH however, the planes are non-centrosymmetric, as figure 1 shows, due to the monoclinic distortion and the resulting cross-terms in the exchange Hamiltonian lead to a Dzyaloshinsky-Moriya (DM) antisymmetric exchange interaction. This interaction is significant in CFTH being of order $(\Delta g/g)J$ where Δg is the departure of the g -value from the free-ion value. SC determined [9, 10] that the dominant contribution to line-broadening in CFTH arises from the phonon-modulated DM interaction and that in this situation the linewidth is also linear in T when $T \gg T_N$. Further support for the existence of a DM interaction in this compound comes from spin-wave measurements [12] which showed a gap of 0.6 meV at the $(0 -1 1)$ antiferromagnetic zone centre. This gap probably arises from a DM interaction [7, 9, 10], although we proposed alternative corrections to the Hamiltonian.

SC fitted ΔH , the linewidth measured in Gauss, to the empirical form of equation (2).

$$\Delta H = \alpha + \beta T + \frac{\gamma}{[T - T_N]^n} \quad (2)$$

where α is the linewidth extrapolated to $T = 0$ from the linear region above 70 K and β the gradient in this region arising from the antisymmetric exchange. The third term is only important very close to T_N and is presumed to result from the onset of critical fluctuations which we previously observed in the deuterated material using neutron scattering [11]. We determined α to be 42 ± 1 G and β to be 0.78 ± 0.03 G K⁻¹. SC also proposed that the best approximation for the shape of the resonance was a Lorentzian times an exponential although the exact form of the lineshape is unimportant when $J^2 \gg M_2$. We used a Lorentzian lineshape at all temperatures because it was found to give a reliable value for the linewidth.

3.2. Effect of doping on linewidth

We observed that as the concentration of the magnetic ion decreased both α and β in equation (2) decreased leading to a reduction in the linewidth at a particular temperature. The decrease of α was the more significant. Since the linewidth calculated by SC is linear in the number of magnetic neighbours of a particular ion, a decrease in the number of magnetic neighbours of some of the ions will be expected to reduce the linewidth. The decrease in the minimum linewidth as the concentration of the magnetic ion decreases is shown in figure 5.

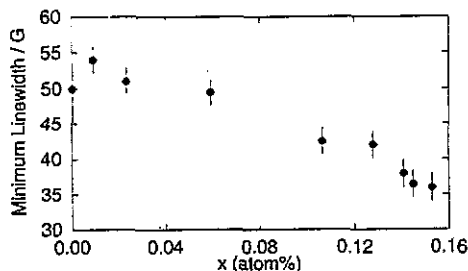


Figure 5. The dependence of the minimum ESR linewidth of doped CFTD on the dopant concentration.

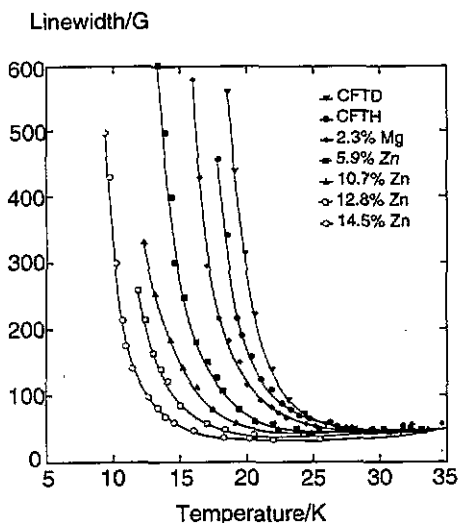


Figure 6. The dependence of the ESR linewidth of each of the doped samples on temperature in the region of T_N . The graph shows how accurately one can determine the differences in T_N of compounds with different dopant concentrations.

3.3. Effect of doping on T_N

Figure 6 shows the FWHM of the ESR signal of each sample plotted against temperature in the region around T_N . Due to the weakness and broadness of the signal at temperatures very close to T_N , it was difficult to determine accurately the absolute value of T_N . For the pure material, T_N was estimated to be the temperature at which

the resonance could just be discerned at the maximum sensitivity of the instrument. This was 16.1 ± 0.1 K, which compares favourably with previous measurements. All the samples showed the same rapid linear increase in ΔH in the transition region and hence the differences in T_N could be determined to within 0.2 K.

A plot of $T_N(x)/T_N(0)$ against the fractional concentration, x , of the diamagnetic dopant is shown in figure 7. This was found to be very sensitive to the difference in values of T_N but very insensitive to the actual values chosen for T_N . The reduction of T_N is linear in x when x is below 0.1 taking the form

$$T_N(x) = T_N(0)(1 - \alpha x) \quad (3)$$

where $T_N(x)$ and $T_N(0)$ refer to the doped and pure material respectively and the constant α is 3.4 ± 0.1 .

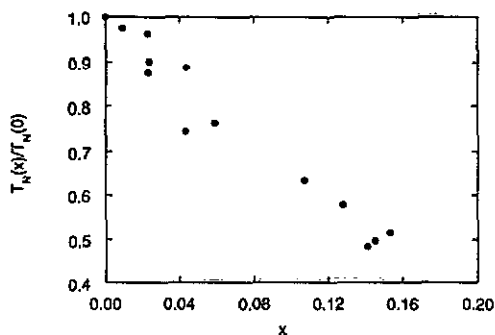


Figure 7. A graph showing the rate at which T_N of CFTH is reduced by doping with the diamagnetic impurities Mg^{2+} and Zn^{2+} . x is the mole fraction of the diamagnetic ion in the samples.

The samples containing 2.25% and 4.32% Zn^{2+} were good quality crystals which gave consistent chemical analyses. However, their linewidth behaviour and hence T_N was sample dependent as figure 7 shows. This behaviour cannot be wholly explained by inhomogeneities in the distribution of the diamagnetic ion which are likely to be much larger in magnetically more dilute samples. Error in positioning the sample in the same place in the temperature gradient of the cryostat by about 2 mm would be required to lead to an error in measuring the actual temperature of up to 2 K, but considering the precautions taken, the error should not be more than a tenth of this. The source of the discrepancy between different crystals grown from the same solution and between these and other samples is difficult to pinpoint.

The transition temperature of the fully deuterated form of the compound, CFTD, is higher than that of CFTH by about 1.2 K. The lattice constant c is slightly shorter in CFTD [5, 6] because deuterium bonding is stronger than hydrogen bonding. This leads to a slightly stronger inter-planar coupling, J' , in CFTD. It is J' which drives the transition to 3D ordering and so T_N is higher in CFTD.

The value of α in equation (3) for CFTH: Zn^{2+} of 3.4 should be compared with values of between 3.0 and 3.5 obtained for other square Heisenberg ferro- and anti-ferromagnets [23, 30, 31]. Comparison of the behaviour of a number of 2D systems, including La_2CuO_4 which has been doped with Mg^{2+} and Zn^{2+} [23], is shown in figure 8. CFTH: Mg^{2+} and CFTH: Zn^{2+} show behaviour very similar to that of other layered Heisenberg systems, including La_2CuO_4 , at low dopant concentrations. As x increases above about 0.1 it appears that T_N is reduced more rapidly in doped CFTH and La_2CuO_4 than in other Heisenberg systems such as K_2CuF_4 and K_2MnF_4 .

This is hard to verify without doping CFTH to higher levels. The fall-off in Zn-doped La_2CuO_4 was originally thought [22, 32] to be faster than in the other 2D Heisenberg systems but this result now appears to be due [23] to the Zn-doped samples inadvertently having different oxygen contents from the pure material. It is clear that the ordering transition temperatures of all the Heisenberg systems decrease much faster on doping than those of Ising systems whose behaviour can be solved exactly. However, the apparently 'universal' behaviour displayed by the Heisenberg systems at low dopant concentrations may be fortuitous [33].

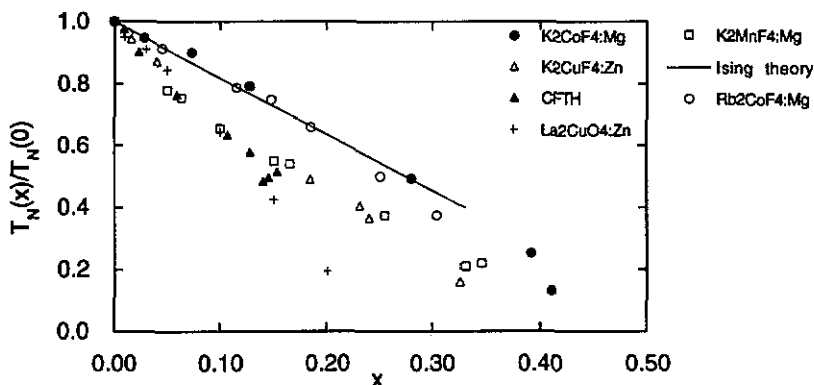


Figure 8. A graph showing the relationship of the results from doped CFTH to those obtained from 2D Ising systems, 2D Heisenberg systems, La_2CuO_4 and from a theoretical treatment of the 2D Ising model. x is the mole fraction of the diamagnetic ion in the sample.

In every 'real' 2D Heisenberg material, long-range order is induced by finite Ising-like anisotropy (as with K_2MnF_4) or finite interplane exchange as in the cases of K_2CuF_4 and La_2CuO_4 . It is likely that CFTH falls into the latter category. In each of the Heisenberg systems the ordering is 3D since a pure 2D Heisenberg system cannot order above 0 K. There appears to be no reason why systems whose ordering is driven by different mechanisms should exhibit 'universal' behaviour in the depression of the ordering temperature by diamagnetic doping. Further, as J'/J is 10^{-4} for K_2CuF_4 [33], 10^{-5} for La_2CuO_4 and less than 10^{-3} for CFTH, it is not necessarily expected that these three systems will show a 'universal' depression of the ordering temperature. We propose that the Heisenberg systems which have been studied so far simply show similar behaviour on doping and that the rate of reduction of T_N is about twice that of the Ising systems. This view is supported by apparent differences in behaviour of different Heisenberg systems when x exceeds 0.1.

4. Conclusions

We have shown that the temperature dependence of the ESR signal of CFTH is a good probe of the way T_N is reduced by diamagnetic doping. This technique could be applied to other compounds whose ESR spectra change rapidly in the vicinity of T_N . The T_N of CFTH is reduced at a similar rate to that of La_2CuO_4 and many other 2D Heisenberg magnets at low dopant concentrations and while this may not represent 'universal' behaviour, it does suggest that the dilution properties of the

quantum systems are not very different from those of the classical analogues. Further studies of other doped 2DHAFs will help to further elucidate our findings.

Acknowledgments

The authors wish to thank Dr Mohamedally Kurmoo of the Royal Institution of Great Britain, London for valuable discussions and assistance with running the ESR spectrometer and Dr Robin Stinchcombe of the Department of Theoretical Physics, Oxford for helpful discussions.

References

- [1] Bednorz J G and Müller K A 1986 *Z. Phys. B* **64** 189; 1988 *Rev. Mod. Phys.* **60** 585
- [2] Birgeneau R J 1990 *Am. J. Phys.* **58** 28
- [3] Manousakis E 1991 *Rev. Mod. Phys.* **63** 1
- [4] Hayden S M, Aeppli G, Osborn R, Taylor A D, Perring T G, Cheong S-W and Fisk Z 1991 *Phys. Rev. Lett.* **67** 3622
- [5] Burger N and Fuess H 1979 *Ferroelectrics* **22** 847
- [6] Kay M I and Kleinberg R 1972 *Ferroelectrics* **4** 147
- [7] Koyama K, Nobumasa H and Matsuura M 1987 *J. Phys. Soc. Japan* **56** 1553
- [8] Seehra M S and Castner T G 1970 *Phys. Rev. B* **1** 2289; 1969 *J. Appl. Phys.* **40** 1240
- [9] Seehra M S and Castner T G 1968 *Phys. Kondens. Mater* **7** 185
- [10] Seehra M S and Castner T G 1971 *Phys. Rev. B* **4** 38
- [11] Clarke S J, Harrison A, Mason T E, McIntyre G J and Visser D 1992 *J. Phys.: Condens. Matter* **4** L71
- [12] Harrison A, Clarke S J, Mason T E and Visser D 1992 *Proc. 1991 Int. Conf. Magnetism; J. Magn. Magn. Mater* **104-7** 557
- [13] Turberfield K C 1967 *Solid State Commun.* **5** 887
- [14] Bird M J and Lomer T R 1971 *Acta Crystallogr. B* **27** 859
- [15] Burger N, Fuess H and Burlet P 1980 *Solid State Commun.* **34** 883
- [16] Matsuura M, Koyama K and Murakami Y 1985 *J. Phys. Soc. Japan* **54** 2714
- [17] Hirakawa K and Ikeda H 1973 *J. Phys. Soc. Japan* **35** 1328
- [18] Regnault L P, Rossat-Mignod J, Villain J and DeCombarieau A 1978 *J. Physique* **39** C6 950
- [19] Yamada K, Kakurai K, Endoh Y, Thurston T R, Kastner M A, Birgeneau R J, Shirane G, Hidaka Y and Murakami T 1989 *Phys. Rev. B* **40** 4557
- [20] Chakravarty S, Halperin B I and Nelson D R 1988 *Phys. Rev. Lett.* **60** 1057; 1989 *Phys. Rev. B* **39** 2344
- [21] Tyč S, Halperin B I and Chakravarty S 1989 *Phys. Rev. Lett.* **62** 835
- [22] Chakraborty A, Epstein A J, Jarrell M and McCarron E M 1989 *Phys. Rev. B* **40** 5296
- [23] Cheong S-W, Cooper A S, Rupp L W, Jr., Batlogg B, Thompson J D and Fisk Z 1991 *Phys. Rev. B* **44** 9739
- [24] Okada K, Kay M I, Cromer D T and Almadovar I 1966 *J. Chem. Phys.* **44** 1648
- [25] Shimada J, Abe H and Ōno K 1955 *J. Phys. Soc. Japan* **11** 137
- [26] Benner H and Boucher J P 1990 *Magnetic Properties of Layered Transition Metal Compounds* ed L J de Jongh (Dordrecht: Kluwer Academic)
- [27] Bencini A and Gatteschi D 1990 *EPR of Exchange Coupled Systems* (Berlin: Springer)
- [28] Richards P M and Salamon M B 1974 *Phys. Rev. B* **9** 32
- [29] Seehra M S 1969 *Phys. Lett.* **28A** 754
- [30] Breed D J, Gilijamse K, Sterkenburg J W E and Miedema A R 1973 *Physica* **68** 303; 1970 *J. Appl. Phys.* **41** 1267
- [31] Idogaki T and Uryū N 1978 *J. Phys. Soc. Japan* **45** 1498
- [32] Xiao G, Cieplak M Z and Chien C L 1990 *Phys. Rev. B* **42** 240
- [33] de Jongh L J 1990 *Magnetic Properties of Layered Transition Metal Compounds* ed L J de Jongh (Dordrecht: Kluwer Academic) pp 31-47