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The effect of spin dilution on magnetism of the linear chain system β-$Cu_{2-x}Zn_xV_2O_7$

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Abstract. We have measured the magnetic susceptibility (χ) and heat capacity (C_p) of β-$Cu_{2-x}Zn_xV_2O_7$ ($x = 0$, 0.05, 0.1, 0.15, 0.2, 0.3, 2) in the temperature range 2–300 K. A one-dimensional alternating exchange Heisenberg antiferromagnetism (HAF) is observed in all compositions with chains of infinite length. The intra-chain exchange remains uniform and decreases marginally with dilution of the magnetic state. A cooperative ordering is seen in the magnetic chains for all Zn concentrations ($x \leq 0.3$). The temperature of occurrence of this transition decreases with increasing Zn concentration. Though the conventional spin-wave theory has been used here to describe the properties of the ordered phase, the presence of some contributions like the lattice heat capacity in C_p and the Curie–Weiss term in susceptibility introduces some uncertainties in the estimation of the proportions contributed by the spin system. Therefore, the nature of the ordered phase could not be ascertained unambiguously.

Keywords. Antiferromagnetics; spin chains; spin waves; magnetic properties.

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1. Introduction

Study of one-dimensional (1D) systems has progressed remarkably in the past few decades. These systems have gained enough importance from the fundamental point of view due to their simple magnetic structures where the spin-Hamiltonians can be solved exactly. New discoveries like spin-Peierls transition [1], Haldane gap [2], spin-ladders [3] etc. have multiplied the attraction towards these systems. The widely different magnetic behaviours of integer and half-odd-integer spin-1D systems [4] have added some more charm to this saga. Experimentally, Ni-based compounds exhibit the Haldane gap because of the integer spin carried by this ion ($3d^8$) while a lot of attention has been focussed on compounds of copper and vanadium that carry the $3d^9$ and $3d^1$ configurations respectively for the latter class of spin systems. Earlier compounds like $CuCl_2 \cdot 2NC_5H_5$, $KCuF_3$ [5], $Cu(NH_3)_4NO_3$

[6] were discovered to exhibit a spin-singlet ground state but recently the focus has been shifted to the oxides of these metals like $CuGeO_3$ [1], $CuSiO_3$ [7], $SrCu_2O_3$ [8], $BaCu_2V_2O_8$ [9], $(VO)_2P_2O_7$ [10], and NaV_2O_5 [11] where together with the singlet ground state strong quantum spin fluctuations have also been observed.

Recent studies [12–14] on the correlation of structure with magnetism in the thortveitite ($M_2V_2O_7$, M = transition metal) type materials have drawn considerable attention. Besides a layered structure, M–O–M chains are found in most of the Cu-based compounds, which consequently exhibit low-dimensional behaviour. In $Cu_2V_2O_7$, vanadium is present in a nonmagnetic ($3d^0$) state. Out of the two crystallographic forms of this compound, Cu atoms are packed linearly in the β-phase (monoclinic with space group C2/m) with the V–O chains separating them. The crystal structure of this phase shows unequal bond lengths and bond angles on the two sides of each Cu atom [15]. Therefore, the exchange interaction of a Cu ion with its neighbours on the two sides is not expected to be equal. Instead, an alternating exchange spin-$\frac{1}{2}$ linear chain model (ALE) is expected to describe this situation more appropriately. Touaiher *et al* [12] observed the susceptibility of β-$Cu_2V_2O_7$ to drop sharply at low temperatures implying the presence of a spin-gap but they attributed the gap to arise from the dimerization of the Cu ions. Pommar *et al* [14] observed α-$Cu_{2-x}Zn_xV_2O_7$ (orthorhombic with space group Fdd2) to undergo a structural phase transition to the β-phase at $x > 0.15$. From the magnetization measurements they inferred the α-phase to be a canted antiferromagnet at low temperatures and the β-phase to be a linear chain antiferromagnet with a uniform intrachain interaction at high temperatures. In compositions with $x \geq 0.2$, Pommer *et al* also observed a small kink in the susceptibility below ∼22 K and attributed it to the cooperative ordering of the chains. Using only the EPR data they inferred this order to be three-dimensional. In order to further explore the nature of the ordered phase and better understand the magnetic properties of the β-phase in the hitherto unexplored region ($0 < x < 0.2$) of Zn concentration, we have measured the magnetic and thermal properties of the series β-$Cu_{2-x}Zn_xV_2O_7$. We have systematically varied the concentration of Zn (x = 0, 0.05, 0.1, 0.15, 0.2 and 0.3). In the parent composition, the susceptibility and specific heat data reveal the presence of chains with a uniform intrachain exchange interaction implying thereby the absence of the spin gap. Upon dilution of the magnetic sites, the exchange interaction remains uniform but its strength reduces slightly. Though the chains remain independent of each other at temperatures above the temperature of the hump, a cooperative ordering is observed at low temperatures where a 3D spin-wave theory is attempted to describe the properties. Though at these doping levels the chains are expected to be of short lengths, segmentation effects are not observed as the measured magnetic and thermal properties agree satisfactorily with the infinite chain models.

2. Experimental details

The standard ceramic route was chosen to synthesize powder samples of $Cu_{2-x}Zn_xV_2O_7$ (x = 0.0, 0.05, 0.1, 0.2, 0.3). Zn-free samples were formed in α-phase when sintered at 650°C and in β-phase when sintered at 750°C.

However, in Zn-doped samples the β-phase was formed at lower sintering temperatures (∼650°C). Powders were pressed into rectangular pellets using the binding agent, polyvinyl alcohol (PVA), heated at the respective sintering temperatures and quenched directly to room temperature. This process (pelletizing and quenching) had to be repeated a number of times to get samples of single phase. The phase purity was confirmed from their X-ray diffraction patterns taken with a Philips PW diffractometer using CuKα radiation and magnetization measurements. Lattice parameters were refined using Rietveld method (RIETAN 2000). DC magnetization in an applied field of 5 kOe and heat capacity in zero fields were measured in the temperature range $2 \leq T \leq 300$ K with a Quantum Design PPMS.

3. Results and discussions

The XRD data of all the compositions of β-$Cu_{2-x}Zn_xV_2O_7$ (x = 0.0, 0.05, 0.1, 0.15, 0.2, 0.3) could be analysed in terms of a monoclinic lattice with the space group C2/m [15]. The parameters obtained from the Rietveld analysis and their variations with the Zn concentration (x) are in accord with their values in ref. [15].

The susceptibilities ($\chi(T)$) of all compositions are shown in figure 1. No noticeable difference was observed between the ZFC (zero-field-cooled) and FC (field-cooled) magnetization data of all compositions implying thereby the absence of the α-phase in all these compositions. As seen in these plots, all compositions exhibit identical magnetic behaviour. For each composition, $\chi(T)$ displays a broad hump characteristic of a low-dimensional behaviour. As the Zn concentration increases the maximum value of susceptibility ($\chi_{\max}$) increases and the temperature of its maximum ($T_{\max}$) decreases. At temperatures $T > 100$ K susceptibility follows a Curie–Weiss (CW) behaviour in all compositions (see inset of figure 1) with the effective magnetic moment per Cu ion (∼1.9 μ_B) higher than expected (1.73 μ_B) for $s = 1/2$ ion (with $g = 2$) suggesting the presence of an additional magnetic contribution in all the compositions. This is corroborated by the value of g (=2.13 ± 0.02 essentially composition-independent) obtained from the room-temperature ESR spectra of these compositions. However, the interaction between the magnetic ions is antiferromagnetic (AFM) as the Curie temperature (θ) is negative for all compositions. $|\theta|$ decreases with increasing Zn concentration, which suggests a weakening of the magnetic interactions.

For the overlapping concentrations $x = 0.2$ and 0.3, our data agree with that of Pommar *et al* [14] but for the Zn-free sample it does not agree with that reported by Touaiher *et al* [12]. We get a much larger value of $\chi(T)$ at high temperatures ($T > 100$ K), a much slower change in $\chi(T)$ with temperature on both sides of $T_{\max}$ and a value of $\chi_{\max}$ less than half of that reported in [12]. The susceptibility calculated for isolated dimers [16] is also shown in this figure (dashed curve). The present data do not agree with this curve and thus rule out the dimerization of the Cu ions.

The susceptibility (χ_{SPIN}) of a spin-$\frac{1}{2}$ Heisenberg antiferromagnetic (HAF) chain with uniform interactions between the spins was first calculated by Bonner and Fisher [17]. For chains with the exchange constant alternating between the values J_1 and J_2 on the two sides of the magnetic ion, Johnston *et al* [16] calculated χ_{SPIN} and

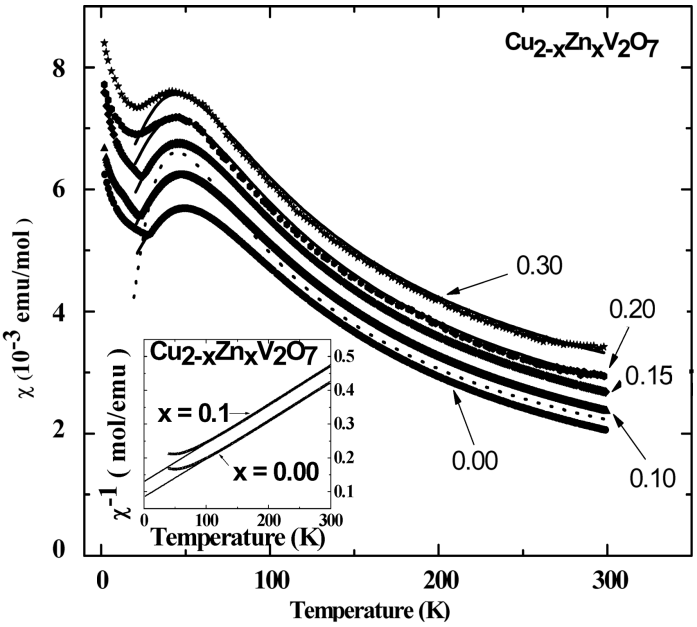

Figure 1. Susceptibility vs. temperature plots of $Cu_{2-x}Zn_xV_2O_7$ for $x = 0.0$, 0.05, 0.10, 0.15, 0.20 and 0.30. Predictions of alternating exchange model are shown by solid curves. The dotted curve represents the susceptibility of the dimers. As shown in the inset, the Curie–Weiss behaviour is followed for temperatures down to 100 K by all these compositions. Some plots in the main panel as well as in the inset have been moved up/down to avoid their overlap with the other plots.

also the heat capacity (henceforth called the alternating exchange (ALE) model) with much higher precision. In this model $\chi_{\rm SPIN}$ is governed by the bond alternation parameter (α) defined as the ratio J_2/J_1. Both these models are valid for chains of infinite lengths. (It may be pointed out that two of the seven polynomials, viz. D_2 and D_3, required for the calculation of $\chi_{\rm SPIN}$ in the ALE model have to be evaluated up to 7th and 10th order respectively. Equation (56g) of [16] prescribes their evaluation up to 4th order only). At temperatures above $T_{\rm max}$ ($\sim$30 K) the data were fitted to these models by varying J_1 and α and keeping g fixed at its experimental value (=2.13). The ALE model gives marginally better agreement with the data than the Bonner–Fisher (BF) model (the Hatfield formula [18] for the BF results is used here). A value greater than 0.98 was obtained for all compositions. Accordingly, α was fixed at 1 and other parameters were varied which resulted in further improvement in the agreement. Solid lines in figure 1 show this agreement. Values of both $\chi_{\rm max}$ and $T_{\rm max}$ also agree with their values predicted by this model. J_1 was found to decrease (from 78 K for $x = 0$) with increasing dilution (to 70 K for $x = 0.3$) of the magnetic site. Thus, despite having unequal bond lengths on either side the Cu ions interact with a uniform exchange. As pointed out by Pommar *et al* [14], there are two unsymmetrical exchange paths

Table 1. Parameters obtained by fitting the susceptibility data to the ALE model at $T > T_{\max}$ and the Curie–Weiss equation at low temperatures ($T < T_N$).

	$T > T_{\max}$				$T < T_N$		
Zn conc. (x)	J (K)	$10^5 \times \chi_0$ e.m.u./mol	$10^3 \times C$ e.m.u./mol-K	$-\theta$ (K)	$10^3 \times \chi_0$ e.m.u./mol	$10^3 \times C$ e.m.u./mol-K	$-\theta$ (K)
0.00	78	9.4	0.55	9.6	5.0	21	12
0.05	77	9.6	0.60	8.2	5.0	19	8
0.1	75	10.2	0.69	9.8	5.3	13.4	8
0.15	72	9.9	0.70	8.4	5.2	20	8
0.2	70	10.1	0.90	2.7	5.8	13.6	8
0.3	70	10.3	0.50	7.6	5.8	15.4	8

(Cu–O–Cu) between two O ions. Consequently, the bond angles of these paths play an equally important role in determining the net exchange constant J_1.

The chains behave independent of each other in this temperature range. Cross-linking between the chains can be studied in terms of a molecular field model where the interchain coupling is represented by a molecular field. No noticeable improvement was observed in the fits by using $\chi_{\rm SPIN}$ corrected by this field [19].

It may be pointed out that a CW contribution was also included in this analysis. However, its presence is doubtful as equally good agreement could be obtained by excluding this term. When included it has a small magnitude ($\sim 5\times10^{-5}$ e.m.u./mol) forming at most 0.01% of the total susceptibility (typically $C \sim 6\times10^{-4}$ e.m.u./mol-K, $\theta \sim -10$ K) and appears to come at the cost of a reduction in χ_0. It has the largest magnitude in the $x = 0.1$ sample and is suspected to arise from the presence of residual amount of the α-phase. Pommar *et al* [14] observed a larger CW term in these compositions and attributed it to the induction of a moment on the Zn ions by the AFM background of the Cu ions. A similar CW susceptibility has also been observed in doped high T_C superconductors where the 2D AFM spin-liquid background was expected to induce a spin moment on the dopant [20,21]. The moments were found on the nonmagnetic ions such as Al, Ga and Zn and were formed by the Cu spins surrounding the dopant site. In $La_{2-x}Sr_x(CuZn)O_4$ a moment ($\mu_{\rm eff}$) $\sim 0.65\ \mu_{\rm B}$ was observed on the Zn ion in the paramagnetic state and decreased considerably in the superconducting state [21]. The near absence of this contribution in the present samples then implies that the AFM background provided by the linear chains is not strong enough to induce moments on the Zn ions. The results of this analysis are summarized in table 1.

At low temperatures, $\chi_{\rm SPIN}$ is known to depend on the length of the chain irrespective of the ends of the chain being open [22] or closed [17]. At high temperatures ($T > J$), $\chi_{\rm SPIN}$ for even chains (finite chains with even number of members in them) is identical to those of the odd chains but starts to depart below this temperature $T \sim J$. Assuming a random distribution of nonmagnetic impurities among the chains, Asakawa *et al* [22] have calculated the average susceptibility of the $s = 1/2$ finite HAF chain system having a uniform exchange. For two of the concentrations studied here ($x = 0.05$ and 0.2) the data do not agree with this model any better

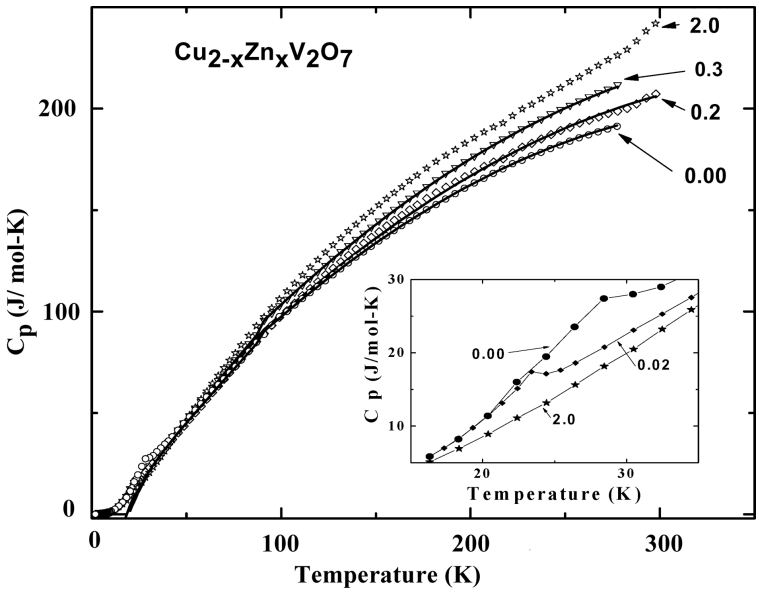

Figure 2. The measured specific heat of some compositions. The solid curves represent the sum of the lattice and magnetic specific heat calculated from the ALE model. The inset shows that the transition temperature decreases with increasing Zn concentration.

than the ALE model implying thereby that the chains are not segmented by the incorporation of Zn.

It is to be noted further that though $\chi(T)$ decreases below $T_{\max}$, it begins to increase upon further cooling after attaining a minimum ($\chi_{\min}$) at $T_{\min}$. Specific heat also shows an anomaly at a temperature roughly coinciding with $T_{\min}$ for all compositions with $x \leq 0.3$. Below $T_{\min}$, susceptibility follows a CW behaviour for all compositions, $\chi(T) = \chi_{0(\mathrm{LT})} + C_{\mathrm{LT}}(T - \theta)$. As shown in table 1, values of the constants χ_0 and C have increased in comparison to their values obtained from the ALE model. A Curie-like upturn has been observed at low temperatures in the paramagnetic region in some of the uniform as well as alternating exchange HAF chain systems; particularly those that contain spin-$\frac{1}{2}$ ions like Cu and V [8,23]. In Ni, Co or some other transition metal compounds, the upturn appears due to the oxygen deficiency in the sample and is absent in the ordered state [24] while in some V-containing samples it was attributed to the segmentation of the chains [25].

The measured specific heats (C_{p}) of these compositions show a monotonic increase with temperature (figure 2). A small peak in the temperature range 20–28 K is observed for compositions $x = 0.00$, 0.2 and 0.3. The peak height decreases as the Zn concentration increases and disappears altogether in the specific heat of the isomorphic compound $Zn_2V_2O_7$ which is expected to be nonmagnetic (see inset of this figure). Estimation of the magnetic contribution (C_{m}) to C_{p} presents some problems as the data for all compositions do not follow the usual Debye or Einstein functions over the extended temperature range, $T_{\max}$–room temperature. Specific heat of the isomorphic compound $Zn_2V_2O_7$ also did not prove to be useful.

Though it fits excellently to a polynomial of sixth degree, the large uncertainties in the values of its coefficients lead to unreliable values of $C_{\rm m}$. Despite the absence of a magnetic contribution, $C_{\rm p}$ of this composition is larger than those of the other compositions ($x \leq 0.3$) at $T > 200$ K. $C_{\rm p}$ is observed to increase with increasing Zn concentration even though the magnetic contribution of all compositions $x \leq 0.3$ remains essentially concentration-independent in this temperature region. Consequently, empirical relations were tried for the estimation of the lattice specific heat ($C_{\rm L}$). In all these compositions, the relations, $C_{\rm L} = AT + BT^2$ for $T > 100$ K and $C_{\rm L} = G + DT + ET^{-2}$ for $30 < T < 100$ K together with C_m calculated from the ALE model [16] gave good agreement with the data at temperatures $T > T_{\rm max}$ (figure 2). These expressions are essentially polynomials of some lower orders (≤ 2) as addition of any higher-order terms did not improve the agreements. The last term (viz. T^{-2}) in the latter expression forms less than 1% of the total value within the interval $30 < T < 100$ K. The obtained values of the coefficients in these expressions varied over a restricted range though a systematic variation could not be seen in those values. Even though $C_{\rm L}$ forms the dominating part of $C_{\rm p}$ in the entire range $30 < T < 300$ K, deviations between the $C_{\rm p}$ calculated with this procedure and its measured value are smaller than $C_{\rm m}$ expected at the corresponding temperature ensuring thereby that the experimental magnetic specific heat, defined by $C_{\rm m}({\rm ex}) = C_{\rm p} - C_{\rm L}$, has been reliably estimated. As shown in figure 3, $C_{\rm m}({\rm ex})$ agrees fairly well with the value calculated from the ALE model for the exchange constant determined from the susceptibility data within this temperature range. For all compositions a narrow hump is observed around 35 K with a height $\approx 0.35R$ and temperature roughly coinciding with their predicted values [17] at $T_{\rm max}(C_{\rm m}({\rm ex})) \approx 0.75T_{\rm max}(\chi)$. The hump appears to be truncated by a rapid increase in $C_{\rm m}({\rm ex})$ with decreasing temperature which is considered to be a precursor to a transition at a lower temperature.

Both the susceptibility and the specific heat do not reveal an unequivocal picture of the magnetic state at lower temperatures, $T < 20$ K. Nonetheless the thermal data reveal that the chains do not remain independent of each other at these temperatures. For noninteracting chains, Bonner and Fisher [17] have shown the magnetic specific heat ($C_{\rm m}$) to vary as FT with the coefficient $F \sim 80$ mJ/mol-K^2 calculated for the value of the exchange constant determined above and is much larger than the total specific heat ($C_{\rm p}$) observed in these compositions at $T < 5$ K. $C_{\rm p}$ follows a T^3 dependence for all compositions at these temperatures (figure 4). Apparently the observed cusp in $C_{\rm p}$ represents a transition to the ordered state. Assuming the ordering to be 3D in nature, spin-wave theory (SW) predicts $C_{\rm m}$ (for 3D HAF magnons) to have the same [26] dependence on temperature as that of the phonons, viz. T^3, at these temperatures making it impossible to separate the two contributions. However, we noted that within this temperature region ($T < 20$ K) the Debye function for $C_{\rm L}$ (with $\theta_{\rm D}$ (Debye temperature) $\sim$249, 251, 252 and 269 K for $x = 0.00$, 0.2, 0.3 and 2 respectively) along with a T^3 magnon contribution [26] gave a marginally lower RMS deviation than T^3 alone. Therefore it is considered as the correct representation of $C_{\rm L}$. The Debye curve was further extrapolated manually to temperatures within the interval 20 K $\leq T \leq$ 30 K such that it smoothly joined the curve at $T > 30$ K. $C_{\rm m}({\rm ex})$ thus obtained shows a λ-like anomaly which is the signature of a long-range order occurring in the sample. $C_{\rm m}({\rm ex})$ obtained here

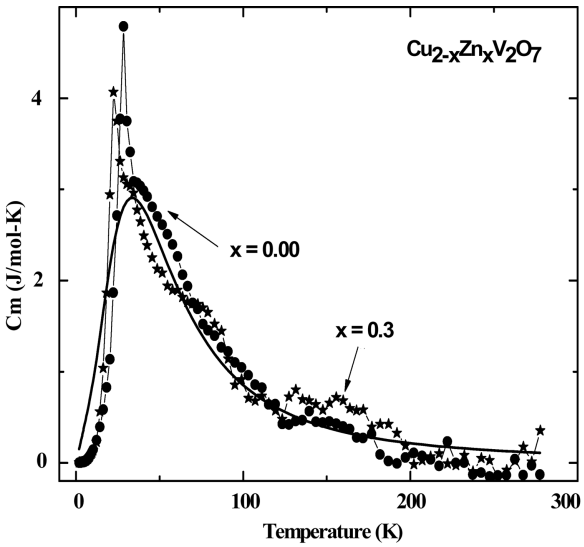

Figure 3. The magnetic specific heat of compositions $x = 0.0$ and 0.3. Predictions of the alternating exchange model are shown by the solid curve. $C_{\rm m}$ of other compositions are not included to avoid congestion.

is believed to be the best estimate that can be obtained under the conditions mentioned above. It gives the entropy of the spins (from 2 K to ∞) close to the value expected from theory (5.78 cal/mol-K) although somewhat large error is involved in this value (due primarily to the large uncertainties in $C_{\rm L}$ within the transition region). (It may be pointed out that the T^3 dependence for $C_{\rm L}$ also produces the λ-like anomaly but it yields slightly larger entropy). $T_{\rm N}$ decreases with increasing dilution of the Cu sites. The peak height also reduces as is observed in figure 2 from the $C_{\rm p}$ data.

In polycrystalline samples at low temperatures ($T < T_{\rm N}$), $\chi(T)$ within the SW regime [26] is predicted to be essentially temperature-independent: $\chi_{\rm SW} = 2/3\chi_{\perp}(0)$ with $\chi_{\perp}(0) = Ng^2\mu_{\rm B}^2/2zJ$ as the parallel susceptibility diminishes rapidly ($\propto (T/zSJ_{\rm 3D})^2$) with decreasing temperature. Though such a behaviour is not observed below 20 K, from the CW behaviour observed in this temperature range we note that $\chi_{0({\rm LT})} \sim \chi_{\rm SW}$ for the J values obtained above. It suggests that the Cu ions continue to follow the SW behaviour and that the paramagnetic behaviour arises due to the presence of some other species of ions. At low temperatures the Cu–O–Cu correlation length ($\xi_{\rm 3D}$) is expected to be several times larger than the interionic spacing. All Cu ions in a chain are therefore expected to remain coupled with each other despite a (/few) Zn ion(s) separating them (such as the Zn ion in the chain Cu–O–Zn–O–Cu) and thereby provide an infinite medium to the spin-waves (which consequently display the T^3 dependence of $C_{\rm m}$). A large $\xi_{\rm 3D}$ further suggests that these correlations may surround the foreign ion situated within the chains. Consequently, such foreign ions are likely to have very little interaction with other similar ions and are also likely to be affected by the AFM background. Zn ions may be responsible for the paramagnetic behaviour observed below $T_{\rm N}$ with

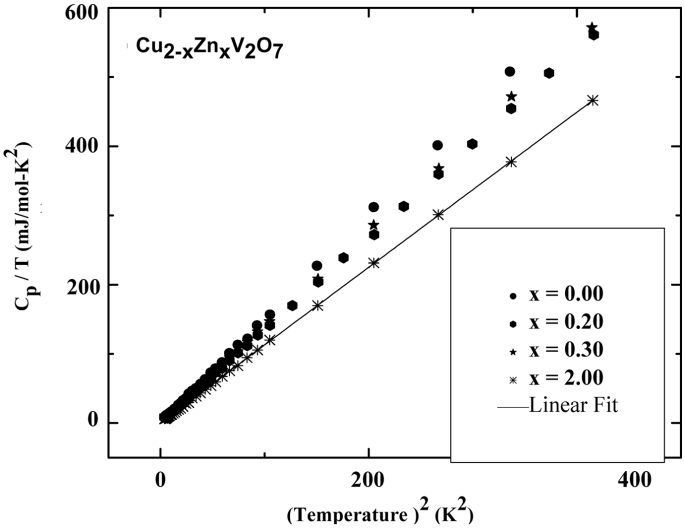

Figure 4. The low temperature behaviour of specific heat.

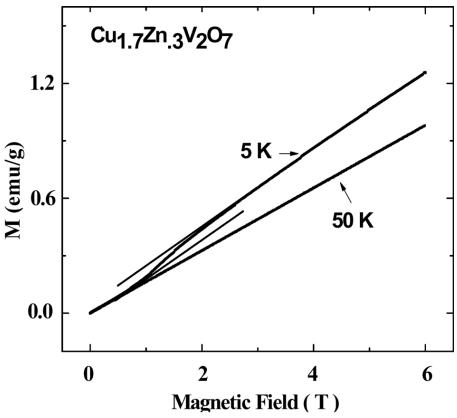

Figure 5. Field dependence of magnetization shows the spin-flip transition.

the required moment being induced by the AFM background formed by the Cu spins [20]. The observed value of $C_{\rm LT}$ yields an effective moment, $\mu_{\rm eff} \sim 0.5\ \mu_{\rm B}$ per Zn ion which agrees well with that observed in the high $T_{\rm C}$ compounds [20]. No such moment was observed at high temperatures ($T > T_{\rm max}$) and corroborates the conclusion drawn above that the 1D correlations among the Cu ions are not strong enough to induce a moment on Zn.

The field dependence of magnetization $M(B)$ measured at 5 K (figure 5), also reveals an AFM magnetic order to be present in the samples. The initial slope of this curve equals the $T = 5$ K susceptibility shown in figure 2. A small jump in $M(B)$ can be observed at $B_{\rm sf} \sim 1.1$ T which is attributed to the spin-flip transition. With increasing field, $\mathrm{d}M/\mathrm{d}B$ increases rapidly and shows a peak at ∼1.1 T. However,

above the peak it decays gradually and attains a steady value at $B > 3$ T. On the other hand, no such jump is observed in $M(B)$ at ∼50 K which continues to increase linearly with B. In the crystalline samples, the spin-flip transition exhibits a sharp peak in the measured susceptibility while in the polycrystalline samples it is a continuous process yielding a short and broad peak [27]. Consequently, the uncertainties in the determination of $B_{\rm sf}$ are large in the polycrystalline samples. Within these large uncertainties, $B_{\rm sf}$ determined here appears to be independent of temperature at $T < T_{\rm N}$ and its value compares favourably with the corresponding value in other AFM compounds, e.g. 0.6 T in $CuCl_2 \cdot 2H_2O$ ($T_{\rm N} \sim 4.3$ K) [28] and 4 T in $CaCu_2O_3$ ($T_{\rm N} \sim 66.5$ K) [27]. The anisotropy constant K calculated from $B_{\rm sf} = \sqrt{2K/(\chi_\perp - \chi_\parallel)}$ [29] yields an anisotropy field $B_{\rm A}$ ($= K/M_0$, M_0 is the sublattice magnetization) of 40 Oe that is equal to its value (38 Oe) calculated from the SW expression $B_{\rm sf} = \sqrt{2B_{\rm E}B_{\rm A}}$. Such a small anisotropy field has negligible effect on the spin-wave spectrum. Consequently, the magnetic specific heat continues to obey the T^3 law.

4. Conclusions

We have investigated the magnetic and thermal properties of β-$Cu_{2-x}Zn_xV_2O_7$ for $x = 0$, 0.05, 0.1, 0.15, 0.2 and 0.3. All the compositions exhibit a low-dimensional behaviour that can be described in terms of a uniform exchange 1D infinite chain system. With dilution of the magnetic site, the exchange remains uniform though it decreases slightly. A cooperative ordering is observed at low temperatures for all concentrations of Zn ($x \leq 0.3$). Though the conventional spin-wave theory has been used here to describe the properties of the ordered phase, the presence of some additional contributions like the Curie–Weiss term in susceptibility and the lattice heat capacity in $C_{\rm p}$ introduces some uncertainties in the estimation of the proportions contributed by the spin system. Therefore, the nature of the ordered phase could not be ascertained unambiguously. The infinite-chain behaviour observed in the magnetic and thermal properties at high temperatures further suggests that the incorporation of Zn does not segment the chains in all compositions. Though the magnetic (Cu–Cu) correlation length increases with decreasing temperature, apparently it exceeds the interionic distance such as Cu–O–Zn–O–Cu in all these compositions even at room temperature. As the AFM correlations amongst the Cu spins surround the Zn ions, these ions remain uncorrelated with the Cu ions and may be responsible for the Curie–Weiss behaviour observed in the ordered state.

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