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Zn₂VO(PO₄)₂: an $S = 1/2$ Heisenberg antiferromagnetic square lattice system

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Abstract

We have reinvestigated the magnetic properties of Zn₂VO(PO₄)₂ by means of magnetic susceptibility $\chi(T)$ and specific heat $C_p(T)$ measurements performed on polycrystalline samples. At high temperatures $\chi(T)$ follows a Curie–Weiss law with the effective moment expected for a V⁴⁺, $S = 1/2$ ion, while a rounded maximum in $\chi(T)$ at 6.95 K and a hump in $C_p(T)$ around 4.5 K indicate the onset of antiferromagnetic correlations at low temperatures. Finally, a kink in $\chi(T)$ and a well defined mean-field anomaly in $C_p(T)$ at $T_N = 3.7$ K evidence a transition into an ordered antiferromagnetic state. A comparison of $\chi(T)$ and of the magnetic contribution $C_p^{\text{magn}}(T)$ to the specific heat with theoretical predictions indicates that the magnetic lattice of this compound corresponds to a square lattice rather than the spin chain proposed in an earlier report. The results of quantum Monte Carlo calculations for a square lattice agree very well down to T_N with $C_p^{\text{magn}}(T)$ extracted from our experiment, while finite size calculations overestimate the specific heat in the region of the maximum in $C_p^{\text{magn}}(T)$.

1. Introduction

Low dimensional, low spin systems are currently of strong interest because enhanced quantum fluctuations lead to unusual ground states and unusual low temperature properties. One of the cases most studied in the past few years is that of an $S = 1/2$ Heisenberg antiferromagnetic square lattice, because of its relevance for high temperature superconductivity (HTSC) in cuprates. While a huge amount of data have been accumulated for these compounds (see e.g. [1]), their very large in-plane exchange $J_{2D} > 1000$ K prevents the investigation of some properties, e.g., a detailed analysis of the magnetic specific heat at temperatures of the order of J (because, at those temperatures, the total specific heat is completely dominated by the phonon contribution), or the properties in an applied field H of the order of J (since the corresponding fields are one order of magnitude larger than the available laboratory fields). Thus finding

examples of square lattice systems with a low interaction strength of the order of 10 K is still of strong interest.

In the early days it was argued [2] that the quantum fluctuations lead to the formation of a new disordered, spin liquid state in a square lattice. However it is now widely accepted that at $T = 0$ K they order in a Néel state [1]. Theoretical studies suggest that by introducing a frustrating diagonal antiferromagnetic exchange J_2 , one might recover a spin liquid state at some critical values of the frustration parameter $\alpha = J_2/J_1 \approx 0.5$. While the corresponding theoretical model, the J_1 – J_2 model, has been widely investigated [3], experimental realizations are very scarce, currently restricted to two families of compounds, Li_2VOXO_4 ($X = \text{Si}, \text{Ge}$) [4–6] and $\text{AA}'\text{VO}(\text{PO}_4)_2$ ($A, A' = \text{Pb}, \text{Zn}, \text{Sr}, \text{Ba}$) [6, 7], none of them being in the interesting spin liquid range. Therefore there is currently a strong interest in finding new candidates for the frustrated square lattice spin system. In a search for such systems, our attention was drawn to $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ [8]. An earlier investigation proposed it to be a spin chain system [9], but after analysing its structure and possible superexchange paths, we instead suspected this compound to be a square lattice, with a possible frustrating diagonal exchange of the appropriate strength. We therefore synthesized $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ and investigated its magnetic properties.

2. Experimental procedure

Polycrystalline $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ was prepared by solid state reaction between $\text{Zn}_2\text{P}_2\text{O}_7$ and VO_2 in a flowing argon atmosphere at 900°C . $\text{Zn}_2\text{P}_2\text{O}_7$ was, in turn, obtained by reacting $\text{NH}_4\text{H}_2\text{PO}_4$ with ZnO in air at 600°C . X-ray diffraction data obtained from the polycrystalline powder indicated that the sample was single phase within the limits of x-ray diffraction. Magnetization and specific heat measurements were made using commercial equipment: a magnetic property measurement system (MPMS) and a physical property measurement system (PPMS), respectively, both from Quantum Design.

3. Results and discussion

3.1. Structural aspects

The existence of $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ was first reported by Lii *et al* [8]. This material crystallizes in the tetragonal space group $I4cm$ with cell parameters $a = 8.9227(13)$ Å and $c = 9.039(3)$ Å. Our view of this structure is that it is formed of VO_5 square pyramids connected by ZnO_5 square pyramids and PO_4 tetrahedra forming layers perpendicular to the crystallographic c -axis. One such layer is shown in figure 1. The VO_5 square pyramid is regular with the vanadium ion displaced from the basal plane towards the apex oxygen. The V–O1 bond length is 2.02 Å, O1 being one of the four equivalent oxygen ions forming the base of the pyramid. The distance from V^{4+} to the apex oxygen (O2) is much shorter, only 1.57 Å, and indicates the formation of a vanadyl double bond. As will be discussed later, the orientation of this vanadyl bond is very important for the magnetic properties. Within a layer, the nearest neighbour (NN) VO_5 pyramids are connected by corner-sharing PO_4 tetrahedra while next nearest neighbour (NNN) VO_5 pyramids are connected by two ZnO_5 square pyramids which share an edge to form a dimer. In a given layer, the VO_5 pyramids and the PO_4 tetrahedra point in the same direction, while the ZnO_5 pyramids point in the opposite direction. All the V^{4+} ions are arranged along a line parallel to the c -axis (figure 2).

In the earlier reports [8, 9] $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ was described as formed of one-dimensional chains of VO_6 octahedra, linked by corners along the c -direction. Indeed the shortest V–V

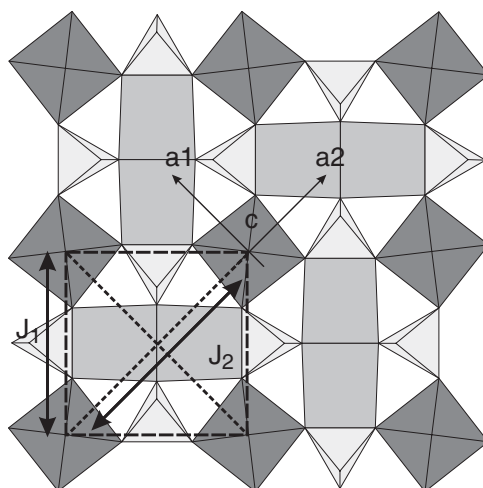


Figure 1. Structure of Zn₂VO(PO₄)₂ projected along [001] showing a single layer of VO₅ square pyramids (dark grey), and their connectivity through PO₄ tetrahedra (light grey) and ZnO₅ square pyramids (light grey squares). J_1 and J_2 indicate the possible intralayer exchange interactions between magnetic V⁴⁺ ions.

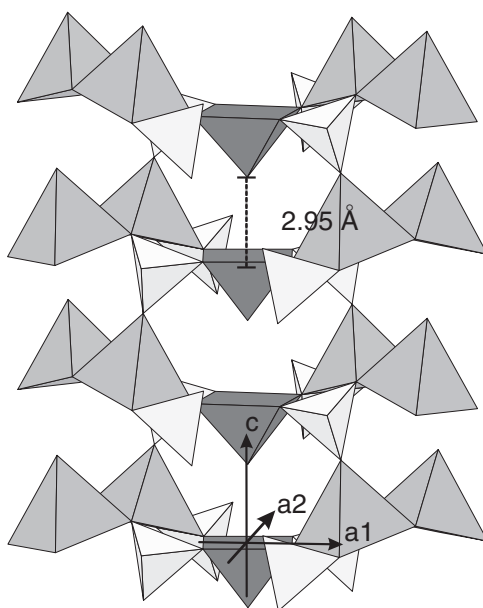


Figure 2. Structure of Zn₂VO(PO₄)₂ projected perpendicular to the [001] direction showing the arrangement of VO₅ square pyramids along the c -axis. The same shades as in figure 1 are used with the exception that the ZnO₅ pyramids now appear in a medium grey tone. The distance between the vanadium ions and the *trans*-oxygen ion (see the text) is explicitly shown (2.95 Å).

distance (4.52 Å) occurs along the c -axis while the nearest V–V neighbour distance within a layer (6.31 Å) is significantly larger. Thus taking only V–V distances into account, the description of the structure in terms of vanadium chains seems to be reasonable. However, this approach completely ignores the difference in bonding strengths arising from the different

V–O distances, and the orientation of the occupied d orbital, which are crucial for the magnetic exchange. From a bonding point of view the V–O2 bond length involving the O2 ion located opposite to the vanadyl bond (the so-called *trans*-oxygen) is huge, 2.95 Å (see figure 2), too large for this O2 to be considered as effectively bonded to the vanadium ion. In vanadium oxides an oxygen ion is usually considered as bonded to vanadium when the bond length is smaller than 2.6 Å [10–12]. Thus taking into account the large difference in V–O distance between the vanadyl and the *trans*-oxygen ions, the appropriate V coordination is square pyramidal, and not octahedral.

It is now well established that for V⁴⁺ in both the square pyramidal and such an octahedral coordination, the crystal field splits the low lying triplet t_{2g} such that the lowest lying level is d_{xy}, which lies perpendicular to the vanadyl bond. In Zn₂VO(PO₄)₂, this orbital is also perpendicular to the *c*-axis, and furthermore the distance to the *trans*-oxygen ion, which would have to transfer the magnetic exchange along the *c*-direction, is large. Then one expects the exchange along the *c*-direction to be very weak. On the other hand, the d_{xy} orbital allows an obvious exchange path through the PO₄ tetrahedra to the next neighbour in the plane. In the past few years it has been shown that magnetic exchange through such PO₄ tetrahedra can be quite strong [13–16]. If this NN exchange J_1 were to be dominant, the spin system would correspond to a square lattice system. But the d_{xy} orbital would also allow a NNN superexchange J_2 through the ZnO₅ pyramids. From empirical considerations, it is not possible to anticipate the relation between J_1 and J_2 on the basis of structural considerations and thus we decided to experimentally investigate the magnetic properties of this material in order to identify its magnetic lattice.

3.2. Magnetic susceptibility results

Figure 3 shows the temperature dependence of the magnetic susceptibility $\chi(T)$ measured in two different fields, $H = 1000$ Oe and $H = 1 \times 10^4$ Oe. $\chi(T)$ presents a behaviour typical of a low dimensional spin system, with a Curie–Weiss-like increase below room temperature, ending in a broad maximum at $T_{\max}^{\chi} = 6.95$ K which corresponds to the onset of antiferromagnetic short range correlations. A small kink in $\chi(T)$ at $T_N = 3.75$ K points to a transition to a three-dimensional antiferromagnetic ordered state. The increase of $\chi(T)$ below T_N when the field is raised from 1000 Oe to 1×10^4 Oe indicates that a spin-flop-like transition takes place at some field between these values. This behaviour is typical for antiferromagnetic order in a low dimensional system with a weak spin anisotropy [17].

In order to obtain a quantitative estimate of the strength and geometry of the magnetic interactions present in Zn₂VO(PO₄)₂ we successively fitted our polycrystalline $\chi(T)$ data with different theoretical models. We first fitted the high temperature data (above 34 K) with the simple Curie–Weiss model (equation (1)).

$$\chi(T) = \chi_0 + \frac{C}{T - \theta_{\text{CW}}} \quad (1)$$

where $C = N_A \mu_{\text{eff}}^2 / 3k_B$ is the Curie constant, θ_{CW} is the paramagnetic Curie–Weiss temperature and χ_0 is a small temperature-independent susceptibility. We obtained $\mu_{\text{eff}} = 1.68(1) \mu_B$, $\theta_{\text{CW}} = -6.38(6)$ K and $\chi_0 = -7 \times 10^{-5} \text{ emu mol}^{-1}$. The values indicated in parentheses are the standard deviations of the fitting procedure. The differences between the values for $H = 1000$ Oe and $H = 1 \times 10^4$ Oe fields are of the same order as the standard deviation in each fitting. The result of this fitting procedure is shown in the inset in the upper part of figure 3 as a $1/\chi(T)$ versus T plot (continuous line). The value of μ_{eff} agrees quite well with the spin only value expected for a V⁴⁺ ion, $1.73 \mu_B$. The small and negative Curie–Weiss

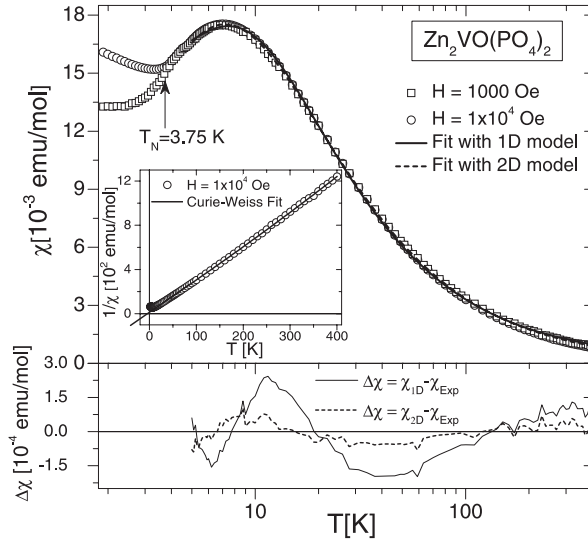


Figure 3. Upper part: magnetic susceptibility data for Zn₂VO(PO₄)₂, measured in an applied magnetic field of 1000 Oe (open squares) and 1×10^4 Oe (open circles) together with the fits with the theoretical model [18] for a 1D spin chain (continuous line) and a high temperature expansion for a 2D square lattice (dashed line; see the text). Inset: $1/\chi(T)$ versus T plot of the $\chi(T)$ data at 1×10^4 Oe (open circles) and the result of the Curie–Weiss fit (continuous line). Lower part: absolute difference between the fitting curves for the 1D (continuous line) and 2D (dashed line) models and the experimental $\chi(T)$.

temperature (θ_{CW}) indicates dominant weak antiferromagnetic exchange, and the small T -independent contribution can be attributed to Van Vleck and diamagnetic contributions.

Next we fitted the $\chi(T)$ data with the theoretical predictions for an $S = 1/2$ Heisenberg spin chain [18] and an $S = 1/2$ Heisenberg spin square lattice. The susceptibility of an $S = 1/2$ Heisenberg spin chain is known for all temperatures with a very high precision from numerical calculations [19–21]. For our fit we used the simple rational function suggested by Feyerherm *et al* [18], given by equation (2):

$$\chi(T) = \frac{C}{T} F\left(\frac{J}{k_B T}\right) \quad (2)$$

with

$$F(x) = \frac{1 + 0.08516x + 0.23351x^2}{1 + 0.73382x + 0.13696x^2 + 0.53568x^3} \quad (3)$$

where $x = J/k_B T$ and C is the Curie constant defined previously. In contrast, the susceptibility of an $S = 1/2$ Heisenberg spin square lattice is less precisely known, especially at low temperatures ($T < J/k_B$). For this fit we used the high temperature expansion series for $1/\chi(T)$ up to the fourth order, as given in equation (4):

$$\frac{1}{T\chi(T)} = \frac{1}{C} \left(1 + x + \frac{x^2}{2} + \frac{x^3}{6}\right). \quad (4)$$

We found that this function reproduces the results of Monte Carlo calculations [22, 23]¹ very well down to surprisingly low temperatures. That the high temperature expansion

¹ Which seem to be currently the most accurate predictions for the susceptibility of a square lattice.

series of $1/T\chi(T)$ up to the fourth term is an excellent approximation for many simple antiferromagnetic spin lattices has already been recognized in the literature [24].

For both fits we included a T -independent χ_0 . The results of these fits are shown in figure 3. In both cases we fitted the data from 400 K down to 5 K. We found that both models reproduce the experimental data very well. However, a detailed analysis (lower part of figure 3) of the differences between the fitting curves and the data clearly shows that the model for the 2D square lattice fits the data systematically better than the model for the 1D chain. This suggests that $\chi(T)$ for $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ is better described by the behaviour expected for a square lattice Heisenberg antiferromagnet. Nevertheless, the differences between the fitting models are not large and thus this analysis does not allow a clear identification of the magnetic lattice of this compound. As shown later, the magnetic specific heat proves that the square lattice is the appropriate model.

The fit parameters are rather similar for the two models with $J_{1\text{D}} = 11.48(1)$ K, $\mu_{\text{eff}} = 1.64(2) \mu_{\text{B}}$ and $\chi_0 = 1.6(2) \times 10^{-4} \text{ emu mol}^{-1}$ for the spin chain model (equations (2) and (3)) and $J_{2\text{D}} = 7.7(1)$ K, $\mu_{\text{eff}} = 1.70(2) \mu_{\text{B}}$ and $\chi_0 = 2.0(5) \times 10^{-4} \text{ emu mol}^{-1}$ for the square lattice model (equation (4)). While the two fits give comparable values for μ_{eff} and χ_0 , the value of the exchange parameter is larger for the chain than for the square lattice, in order to compensate for the lower number of interacting neighbours.

For the square lattice, we made a further fit which included a diagonal exchange J_2 . For this fit we used the high temperature expansion series given by Rosner *et al* [25]. This fit results in a very low J_2 value, of the order of 0.2 K, while J_1 increases only slightly to $J_1 = 7.91$ K, compared to the fit without diagonal exchange ($J_{2\text{D}} = 7.7(1)$ K). This indicates that for $\text{Zn}_2\text{VO}(\text{PO}_4)_2$, the diagonal exchange, and thus the frustration, is very weak and hence not relevant.

3.3. Specific heat results

The temperature dependence of the specific heat of $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ in the temperature range $2 \text{ K} < T < 18 \text{ K}$ is presented in figure 4. The data at higher temperatures are not shown because they are completely dominated by the contribution from the phonons and thus not relevant for discussing the magnetic properties. The magnetic part becomes evident below 10 K as an increase of $C_p(T)$ with decreasing T . This increase leads to a broad hump at around 4.5 K which is related to the onset of low dimensional, short range spin correlations. At $T_{\text{N}} = 3.75$ K a very well defined mean-field-like transition marks the onset of long range antiferromagnetic order. The general dependence on temperature that we observed is rather similar to that reported by Bayi *et al* [9], but, to our surprise, our absolute values are larger by a factor of two for the whole temperature range shown in [9]. As we show later on, a quantitative comparison with theoretical models gives a very strong indication that the absolute values reported by Bayi *et al* cannot be correct, while our data match very well the theoretical results for a square lattice. Furthermore, the T_{N} we observed in our sample is significantly larger than the value $T_{\text{N}} = 3.3$ K reported in the previous work [9]; the size of the anomaly is also larger (even if the previous data are scaled up in order to match our results), and is much sharper. These findings point to a better quality of our sample.

In order to get a quantitative estimate of the magnetic contribution C_p^{magn} to the specific heat, the phonon part C_p^{Phon} was subtracted from the measured total specific heat $C_p(T)$. The specific heat of the phonons was estimated by fitting $C_p(T)$ at higher temperatures ($12 \text{ K} < T < 200 \text{ K}$) with a sum of Debye contributions. Since the magnetic part cannot be neglected for $T < 30$ K, it was accounted for by a term A/T^2 with A being a fitting parameter. Such a term corresponds to the lowest order in $J/k_{\text{B}}T$ in the high temperature expansion series

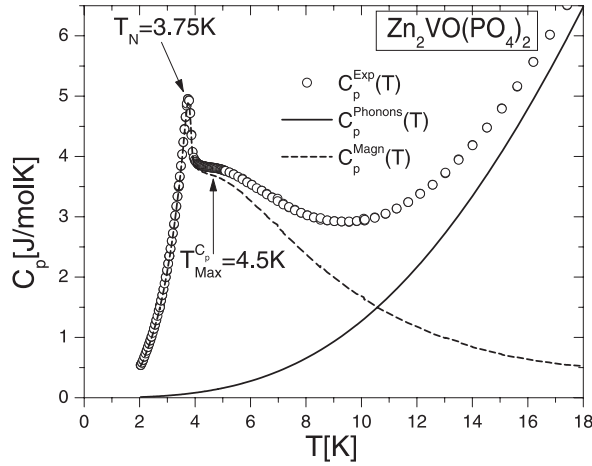


Figure 4. Specific heat data for Zn₂VO(PO₄)₂. The total specific heat (open circles), phonon contribution (solid line) and magnetic contribution (dashed line) are shown separately.

for the specific heat of low dimensional systems. The fit was performed down to 12 K and the final fitting function that we used is given by equation (5) (with $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ the gas constant):

$$C_p(T) = \frac{A}{T^2} + 9R \sum_{n=1}^5 c_n \left(\frac{T}{\theta_{Dn}} \right)^3 \int_0^{\theta_{Dn}/T} \frac{x^4 e^x}{(e^x - 1)^2} dx. \quad (5)$$

Using the resulting Debye temperatures, we extrapolated $C_p^{\text{Phon}}(T)$ down to 2 K and subtracted it from the measured total specific heat, thus obtaining an estimate of $C_p^{\text{Magn}}(T)$. Both $C_p^{\text{Phon}}(T)$ and $C_p^{\text{Magn}}(T)$ are shown in figure 4. As can be seen, $C_p^{\text{Phon}}(T)$ amounts only to a few % of the total specific heat at $T = 4.5 \text{ K}$, the temperature of the hump in $C_p(T)$, while it reaches 50% at 10 K. Accordingly, the absolute value of $C_p^{\text{Magn}}(T)$ at the maximum in the hump is completely insensitive to the estimate of $C_p^{\text{Phon}}(T)$, while above 10 K, $C_p^{\text{Magn}}(T)$ may be sensitively affected by the estimate of $C_p^{\text{Phon}}(T)$. From this fit, we obtained a further estimate of J_{2D} from the value of A , since for a square lattice $A = 3RJ_{2D}^2/8$. We found $A = 171 \text{ J K mol}^{-1}$ and therefore $J_{2D} \simeq 7.41 \text{ K}$ in excellent agreement with the value obtained from the fits of $\chi(T)$ for a 2D square lattice.

We have included in figure 5 the theoretical predictions for $C_p^{\text{Magn}}(T)$ for an $S = 1/2$ spin chain and a square lattice. As for the susceptibility, the former is known up to a high precision from numerical calculations [21]. We used the polynomial approximation of Johnston *et al* [24], and calculated $C_p^{\text{Magn}}(T)$ for the exchange value $J_{1D} = 11.4 \text{ K}$ obtained from the fit of the susceptibility.

In contrast, the theoretical predictions for $C_p^{\text{Magn}}(T)$ for a square lattice became increasingly unreliable when the temperature decreases below J_{2D} . Thus finite size calculations predict a maximum value $C_p^{\text{Magn}}(T_{\text{max}}) = 0.53R$ while quantum Monte Carlo calculations [17, 22, 26] and other approaches combining different techniques [27] converge to a value $C_p^{\text{Magn}}(T_{\text{max}}) = 0.44R$, smaller by 17%. For calculating $C_p^{\text{Magn}}(T)$ for the square lattice we used the recent results of Hoffmann *et al* [28], which were provided to us in tabular form by Uhrig. We scaled these results with $J_{2D} = 7.4 \text{ K}$, obtained from the HTSE fit of the susceptibility. This theoretical result for the square lattice fits very well to the experimental data from high temperatures down to T_N . In contrast, the theoretical results for the $S = 1/2$

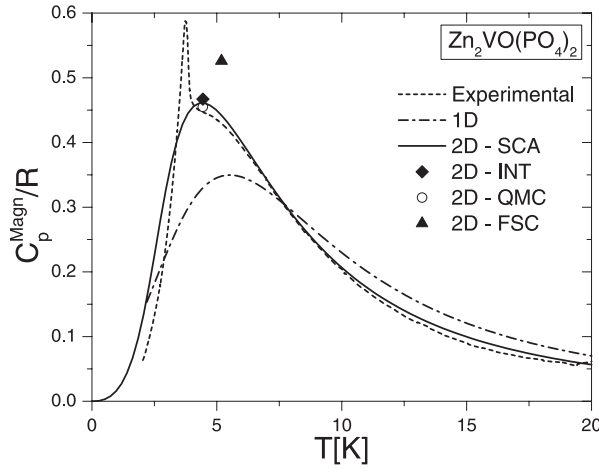


Figure 5. Magnetic contribution to the specific heat of $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ and comparison with theoretical models. 1D corresponds to the result expected for an $S = 1/2$ AF chain, 2D-SCA is the result obtained by scaling the calculations of Hoffmann *et al* [28], 2D-INT, 2D-QMC and 2D-FSC mark the positions of the maximum in $C_p^{\text{magn}}(T)$ determined by an interpolative method [27], quantum Monte Carlo calculations [17, 22, 26] and finite size calculations [3] respectively.

chain deviate considerably from the experimental data at all temperatures. This discrepancy that we observed for the chain cannot be removed by adapting J_{1D} , because the magnitude of the specific heat at the maximum is independent of J_{1D} , and is significantly lower than the experimental results. Thus a comparison of the C_p^{magn} value at the maximum, which is rather insensitive to the phonon contribution, already gives strong evidence for a square lattice instead of a chain. Furthermore, our comparison shows that for a square lattice, finite size calculations overestimate $C_p^{\text{magn}}(T)$ in the range of T corresponding to the maximum, while Monte Carlo and combined approaches seem to be rather accurate.

In summary, this comparison of experimental and theoretical results for the specific heat gives conclusive evidence that $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ is a square lattice, not a one-dimensional chain. Since in a perfect two-dimensional square lattice system the transition towards a long range ordered state takes place only at $T = 0$ K [1], the existence of a finite T_N implies the presence of a weak interaction (J_{\perp}) perpendicular to the layers. From the ratio T_N/J_{2D} one can estimate a value for J_{\perp} . Using the theoretical results of Siurakshina *et al* [29] and our experimental value $T_N/J_{2D} = 0.51$ we obtained a ratio $J_{\perp}/J_{2D} \simeq 0.03$ and thus $J_{\perp} \simeq 0.22$ K. This comparatively small value indicates that the system is quite close to a 2D lattice.

4. Conclusions

Polycrystalline $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ was prepared and characterized as regards its magnetic properties. The ambiguity of $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ being either a spin chain or a square lattice has been sorted out by analysing the combined data on the magnetic susceptibility and specific heat. The nature of the spin lattice in $\text{Zn}_2\text{VO}(\text{PO}_4)_2$ was found to be quasi-two-dimensional. The magnetic structure consists of $S = 1/2$, V^{4+} ions on a square lattice with an antiferromagnetic NN exchange of about 7.4 K, and a much weaker interplane exchange interaction of the order of 0.2 K. We looked for the strength of a possible diagonal exchange between NNN in the plane, but found it also to be much weaker than the NN exchange. The predictions of quantum Monte Carlo and interpolative methods for the magnetic specific heat, C_p^{magn} , of an antiferromagnetic

Heisenberg square lattice agree well with our experimental results, while finite size calculations overestimate this contribution in the region of the maximum in $C_p^{\text{magn}}(T)$.

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