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LETTER TO THE EDITOR

A pseudotetramer in the geometrically frustrated spinel system CdV_2O_4

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Online at stacks.iop.org/JPhysCM/14/L551**Abstract**

The structural and magnetic properties of the geometrically frustrated spinel system CdV_2O_4 with V^{3+} ($S = 1$), whose lattice constant and oxygen u -parameter differ significantly from those of isomorphous MgV_2O_4 and ZnV_2O_4 , have been explored by means of x-ray diffraction and through measurements of the magnetization and nuclear magnetic resonance. CdV_2O_4 undergoes a cubic–tetragonal structural transition with $c_t/a_t = 0.990$ as well as a magnetic transition with a jump of the susceptibility at $T_{c1} = 97$ K. Another magnetic anomaly appears at $T_{c2} = 35$ K which may be a transition to the antiferromagnetic state. The analysis in terms of the high-temperature series expansion of up to eighth order precisely indicates the nearest-neighbour exchange-coupling constant for the cubic phase to be $J = 44$ K. In the vanadium spinel with $S = 1$, the spin-singlet V_4 -tetramer model with the exchange coupling J_{tet} inside V_4 , where $J_{\text{tet}} = 2J$, is applicable at temperatures above $T \approx J_{\text{tet}}$: for CdV_2O_4 with $J_{\text{tet}} < T_{c1}$, all of the susceptibility data for the cubic phase are explained using that model, while for MgV_2O_4 and ZnV_2O_4 with $J_{\text{tet}} > T_{c1}$, it is difficult to account for the data for between J_{tet} and T_{c1} . In this sense, the present bound state may be regarded as *pseudotetramers*.

1. Introduction

Geometrically frustrated spin systems have been investigated for a long time. A state where all pairs of nearest-neighbour spins are aligned in opposite directions is not allowed in such systems and spin correlation is suppressed, so the temperature of the transition to a possible ordered phase is reduced significantly. The system sometimes undergoes a structural phase transition to lower symmetry, since there is a gain of the orbital and magnetic energies on lifting the degeneracy. The triangular $S = 1$ system LiVO_2 with V^{3+} is one such material, where spin-singlet *trimers* are formed [1].

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Table 1. The cubic lattice constants a (Å), the oxygen u -parameters, and selected interatomic distances (Å) and angles (deg) of MV_2O_4 , where $M = \text{Cd, Mg, and Zn}$, at room temperature. The lower row for $M = \text{Zn}$ indicates results based on x-ray four-circle analysis.

M	a	u	V–O	V–V	V–O–V
Cd	8.688(1)	0.394	2.021	3.072	98.95
Mg	8.416(1)	0.386	2.016	2.976	95.14
Zn	8.407(1)	0.385	2.021	2.972	94.66
	8.4027(4)	0.3855(2)	2.016(2)	2.9708(1)	94.90(9)

The normal spinel-type polaronic insulator MV_2O_4 with V^{3+} exhibits a frustration effect [2]. Here, M is a nonmagnetic divalent ion surrounded tetrahedrally by ions such as Mg and Zn (the so-called A site), and V has octahedral coordination (the B site). The network of the V ions is achieved by the linkage of a regular tetrahedron block that has a V ion at each apex, as in the case of pyrochlore-type compounds [3]. On the other hand, LiV_2O_4 with an apparent valence of $V^{3.5+}$ is a metal and it has recently been considered as being a heavy-fermion system at low temperatures [4]. The mechanism of composition-induced metal–insulator transition in the $Li_xMg_{1-x}V_2O_4$ and $Li_xZn_{1-x}V_2O_4$ systems has been investigated from multiple viewpoints [5].

There have been many works on structural and magnetic properties of MgV_2O_4 and ZnV_2O_4 [2, 5–11]. These compounds have similar crystal data and oxygen u -parameters to each other, as shown in table 1. For MgV_2O_4 [2, 6], two magnetic anomalies appear, at $T_{c1} = 65$ and $T_{c2} = 42$ K. At both temperatures, specific-heat anomalies are also present, and at T_{c1} , the cubic–tetragonal transition essentially due to the Jahn–Teller effect occurs. The peak of the specific heat at T_{c2} seems to be too small for a simple magnetic transition. In addition, the susceptibility of the magnetically diluted system $Mg(V_{0.85}Al_{0.15})_2O_4$ with Al^{3+} ($S = 0$) suggests the existence of spin glass. Since this compound does not undergo structural transitions, the anomaly at T_{c1} should be attributed to not only the Jahn–Teller effect, but also a certain kind of spin order. On the other hand, the paramagnetic behaviour at high temperatures was explained in terms of the high-temperature series expansion (HTSE) of up to sixth order with an exchange-coupling constant of about 100 K. It is noted that the nuclear magnetic resonance (NMR) Knight shift for ^{51}V has a temperature dependence *different* from that of the susceptibility and the signal seems to disappear at a temperature close to T_{c1} , possibly due to the spin order [2].

ZnV_2O_4 has properties similar to those of MgV_2O_4 [2, 7, 8]. There is another interpretation in which the magnetic anomalies at T_{c1} and T_{c2} are attributed to the structural transition and the antiferromagnetic one, respectively [7], although the mechanism of change in the paramagnetic state via structural distortion had been unclear until the recent proposal of the theoretical work [11] as introduced below. For the magnetic structures of MgV_2O_4 [9] and ZnV_2O_4 [10], the magnetic moment of the V ion is half the expected value, $2\mu_B$, μ_B being the Bohr magneton, and its direction is parallel to the tetragonal c -axis.

Recently, a tetrahedral mean-field (TMF) theory of the magnetic susceptibility for the spinel sublattice B or the pyrochlore lattice was proposed [12]. Here, the use of the exact solution for the susceptibility for a set of four interacting spins with coupling J_{tet} in the corners of an isolated tetrahedron, in other words, the spin-singlet *tetramer*, is essential, and thus the appearance of a maximum in the susceptibility against temperature has been predicted. The ground-state properties for $S = 1$ were also investigated by breaking up each spin into a pair of $\frac{1}{2}$ -spins [11]. It has been postulated that the twofold degeneracy of the spin singlets of the $S = \frac{1}{2}$ tetrahedron is lifted by the Jahn–Teller effect, which leads to a cubic–tetragonal transition with magnetoelastic interaction.

The present work is a first report on the structural and magnetic properties of CdV_2O_4 , which is isomorphous to MgV_2O_4 and ZnV_2O_4 , based on measurements of x-ray diffraction, magnetization, and NMR. Here, both the cubic lattice constant a and the oxygen u -parameter of CdV_2O_4 are significantly different from those for MgV_2O_4 and ZnV_2O_4 . Therefore, the exchange coupling of CdV_2O_4 may be modified substantially as compared with those of isomorphous compounds. Thus it will become possible to consider physical properties of MV_2O_4 as a function of the exchange coupling. In this work, our attention is mainly focused on the magnetic properties for the cubic phase, and the mechanism of magnetic anomalies is not discussed. In order to estimate the exchange coupling precisely, HTSE up to eighth order is performed, and the application of the spin-singlet V_4 tetramer is examined in detail. These analyses are also done for MgV_2O_4 and ZnV_2O_4 .

2. Experiments

The polycrystalline specimens of MV_2O_4 ($M = \text{Cd}, \text{Mg}, \text{and Zn}$) were prepared by the solid-state reaction method using V_2O_5 (99.99% purity), CdO (99.99% purity), MgO (99.99% purity), and ZnO (99% purity). First, V_2O_3 was made according to the procedure described in [13]. The mixtures of V_2O_3 and MO were pressed into pellets and sealed in evacuated silica tubes, and then heated at 993 K ($M = \text{Cd}$), 1173 K (Mg), and 1073 K (Zn). For MgV_2O_4 , preheating at 993 K was necessary in order to obtain single-phase specimens. The x-ray powder diffraction patterns were taken with $\text{Cu K}\alpha$ radiation and the θ - 2θ scan method in the temperature region between 80 and 300 K. The magnetizations were measured by the Faraday method with a field of up to 1 T at temperatures between 4.2 and 750 (900) K for $M = \text{Cd}$ (Mg and Zn). The magnetic susceptibility was deduced from the linear part of the magnetization-field curve with a decreasing field. The ^{51}V NMR measurements for CdV_2O_4 were also performed with a continuous-wave spectrometer at the Larmor frequency of 14.5 MHz at temperatures from 77 to 400 K.

3. Results and discussion

The cubic lattice constants a of MV_2O_4 , where $M = \text{Cd}, \text{Mg}, \text{and Zn}$, determined in this work are listed in table 1 with the oxygen u -parameters revealed previously [2, 5, 14]. For $M = \text{Zn}$, the results based on x-ray four-circle analysis are added [15]. Selected interatomic distances and angles are also presented. The V-O bond length does not depend on M , since the V valence originates from the critical overlap integral of the V and O atoms. On the other hand, the V-V distance and the V-O-V angle both increase in the sequence $\text{Zn}, \text{Mg}, \text{Cd}$. These composition dependences may be partly attributed to the difference in ionic radii at the A site: 0.78, 0.57, and 0.60 Å for the four coordinations of Cd^{2+} , Mg^{2+} , and Zn^{2+} , respectively [16].

Parts of the x-ray diffraction patterns at 82 and 296 K are shown in figures 1(b) and 1(c). The (440) peak at 296 K splits into two peaks at 82 K with an intensity ratio of about 2:1, whereas the (111) peak at 296 K does not change at 82 K. This result indicates that the crystal system at 82 K may be tetragonal with the axial ratio $c_t/a_t = 0.990$. The temperature dependence of the lattice constant a is shown in figure 1(a). In the heating process, the first-order cubic-tetragonal transition appears at $T_{c1} = 97$ K. This structural anomaly with $c_t/a_t < 1$ is similar to those of MgV_2O_4 [6] and ZnV_2O_4 [7].

The temperature dependences of the magnetic susceptibilities χ for MV_2O_4 with $M = \text{Cd}, \text{Mg}, \text{and Zn}$ are shown in figure 2(a) and the low-temperature parts are indicated in figure 2(b). For CdV_2O_4 , a jump in the susceptibility appears at 97 K, which corresponds to the cubic-

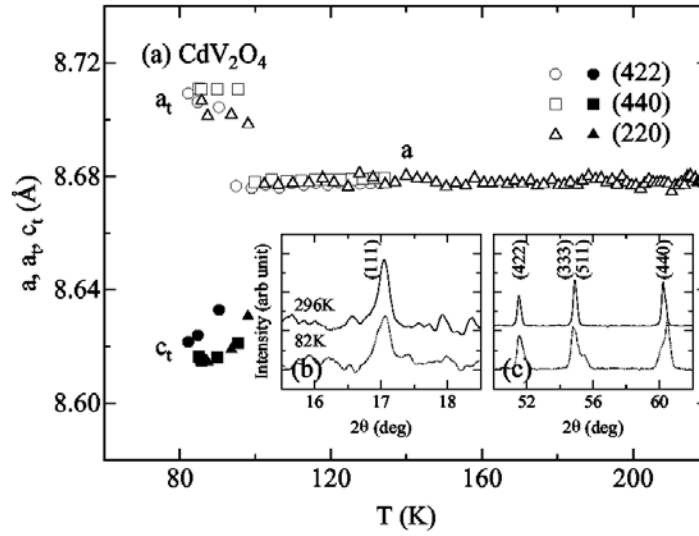


Figure 1. (a) The temperature dependences of the cubic lattice constant a above $T_{c1} = 97$ K and the tetragonal ones a_t and c_t below T_{c1} for CdV_2O_4 estimated from the peaks of (422), (440), and (220) reflections; (b), (c) parts of the x-ray diffraction patterns at 82 and 296 K.

tetragonal transition temperature T_{c1} . At temperatures below T_{c1} , the susceptibility has a broad maximum at 73 K, which is significantly different from the cases of MgV_2O_4 and ZnV_2O_4 . Another anomaly with a change of the temperature derivative occurs at $T_{c2} = 35$ K, which may correspond to the antiferromagnetic order. For $M = \text{Mg}$ and Zn , two anomalies appear, at T_{c1} and T_{c2} , that agree with the previous reports [6, 7]. The present results are summarized in table 2. For all of the compounds, no difference was observed between the susceptibilities for the zero-field-cooled and the field-cooled processes at 1 T.

On the basis of the Heisenberg model,

$$H = J \sum_{\langle i, j \rangle} S_i \cdot S_j \quad (1)$$

where J is the exchange-coupling constant, S is the spin-1 operator, and $\langle i, j \rangle$ denotes a nearest-neighbour pair, the magnetic susceptibility of the spinel sublattice B in terms of HTSE up to eighth order is given as follows:

$$\begin{aligned} \chi^{\text{HTSE}} = \frac{C}{T} [& 1 - 4(J/T) + 12.33333(J/T)^2 - 32(J/T)^3 \\ & + 76.80556(J/T)^4 - 187.4963(J/T)^5 + 478.71677(J/T)^6 \\ & - 1221.6871(J/T)^7 + 2978.22367(J/T)^8] + \chi_0. \end{aligned} \quad (2)$$

Here, C is the Curie constant and χ_0 corresponds to the temperature-independent susceptibility of the Van Vleck orbital and diamagnetic components. The full, dotted, and dot-dashed curves in figure 2(a) denote the results calculated for HTSE up to eighth, seventh, and sixth order, respectively, using parameters listed in table 2. For all of the compounds, C agrees with the value calculated from the spin with $g \simeq 2$; that is, $C \simeq 1$ emu K/(mol V), which may be consistent with a temperature-independent behaviour of the orbital component at the temperatures of interest. The χ_0 -values are comparable to those estimated previously [2]. J for CdV_2O_4 is half of those for MgV_2O_4 and ZnV_2O_4 .

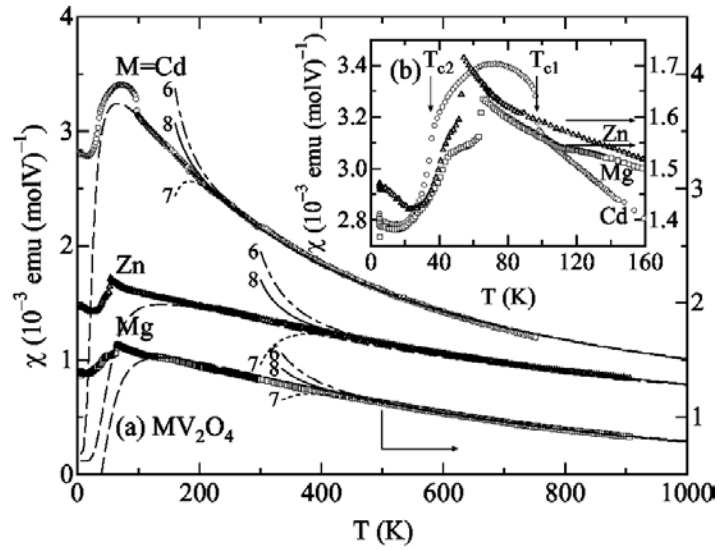


Figure 2. (a) The temperature dependences of the magnetic susceptibilities χ of MV_2O_4 , where $M = \text{Cd}, \text{Mg},$ and Zn ; (b) the behaviours at low temperatures. The full, dotted, and dot-dashed curves in (a) denote results calculated in terms of HTSE up to eighth, seventh, and sixth order, respectively; and the dashed curves indicate fits to the tetramer model, where the parameters used are listed in table 2.

Table 2. The transition temperatures, T_{c1} and T_{c2} (K), and the HTSE and TMF parameters for the magnetic susceptibilities of MV_2O_4 , where $M = \text{Cd}, \text{Mg},$ and Zn ; the Curie constant C (emu K/(mol V)), the constant susceptibility χ_0 (10^{-4} emu/(mol V)), and the exchange coupling J (K) from equation (2); the exchange coupling inside the tetrahedron J_{tet} (K) based on equation (3).

M	T_{c1}	T_{c2}	C	χ_0	J	J_{tet}
Cd	97	35	0.98(2)	1.8(2)	44(1)	82.9(1)
Mg	64.5	45	0.93(6)	1.2(3)	92(7)	175.8(1)
Zn	52	44	0.96(6)	1.1(3)	92(7)	174.6(1)

For the nearest-neighbour interaction between V ions, the direct exchange coupling and the superexchange coupling should be considered. From the V–O distances and the V–O–V angles listed in table 1, if the Anderson-type superexchange coupling is dominant, J for CdV_2O_4 would become more antiferromagnetic. This is not the case. On the other hand, for the case where the direct exchange coupling is the most effective, the composition dependence of J is explained qualitatively, since the V–V distance of CdV_2O_4 is larger than those of MgV_2O_4 and ZnV_2O_4 .

Let us see how the V_4 -tetramer model [12] explains the susceptibility data at temperatures above T_{c1} , although they do not exhibit the maximum phenomenon in the region where the crystal system is cubic. The susceptibility of the tetramer χ^{tet} for the present system is written as

$$\chi^{\text{tet}} = \frac{3C}{2T} \frac{x + 5x^3 + 7x^6 + 5x^{10}}{1 + 6x + 10x^3 + 7x^6 + 3x^{10}} + \chi_0 \quad (3)$$

with $x = \exp(-J_{\text{tet}}/T)$, J_{tet} being as defined before. Here, the interaction outside the tetrahedron is finally assumed to be zero as will be explained later. The dashed curves in figure 2(a) represent fits to equation (3) with J_{tet} listed in table 2, where C and χ_0 are fixed at

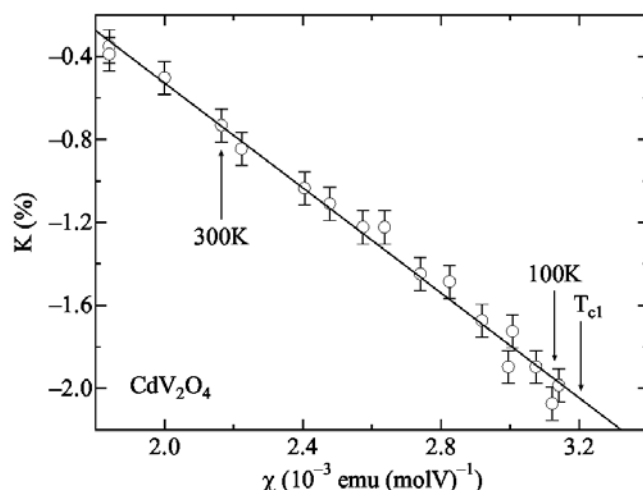


Figure 3. The ^{51}V Knight shift K against the magnetic susceptibility χ of CdV_2O_4 at temperatures above 100 K, where the full line denotes the least-squares fit.

the HTSE values. For $M = \text{Cd}$, the agreement between the experimental and calculated results in the cubic phase is satisfactory. In order to clarify the origin of the susceptibility maximum that appears to be reproduced roughly with this model, the low-temperature structure should be determined precisely. On the other hand, for $M = \text{Mg}$ and Zn , the data above $T \approx J_{\text{tet}}$ are explained by this model, but it is difficult to fit those below J_{tet} . For all of the compounds, J_{tet} is twice J within a standard deviation, which is equivalent to the condition for the high-temperature limit in the TMF model. It should be noted that the finite interaction outside the tetrahedron that has been introduced in [12] does not improve the agreement significantly.

A single resonance line of the ^{51}V nuclei in CdV_2O_4 was observed, although the intensity was very weak. A plot of the Knight shift K against the magnetic susceptibility χ is shown with an implicit parameter T in figure 3. The Knight shift consists of the d-spin component K_d and the Van Vleck orbital one, K_{orb} , which are related to their susceptibilities χ_i ($i = \text{d}$ and orb) through the hyperfine fields A_i as follows:

$$K = K_d + K_{\text{orb}} = \frac{1}{N\mu_B} (A_d \chi_d + A_{\text{orb}} \chi_{\text{orb}}) \quad (4)$$

where N is the number of V ions. The full line in figure 3 provides $A_d = -7.1 \text{ T } \mu_B^{-1}$, $A_{\text{orb}} = 45 \text{ T } \mu_B^{-1}$, and $K_{\text{orb}} = 1.78\%$, using χ_0 listed in table 2 and diamagnetic susceptibilities given in [17]. The magnitude of A_d is comparable to the value for V^{3+} of LiVO_2 [1] and A_{orb} is nearly equal to the free-ion value of the radial average $\langle r^{-3} \rangle$ [18]. This result indicates that the susceptibility presented here is intrinsic and the orbital contribution is temperature independent above T_{c1} , which is consistent with the susceptibility result $g \simeq 2$ described before.

No ^{51}V NMR has been detected at temperatures below T_{c1} . Unfortunately, it is not clear whether the signal disappears or just becomes weaker.

4. Conclusions

The structural and magnetic properties of the spinel-type CdV_2O_4 have been revealed. The cubic-tetragonal structural phase transition with $c_t/a_t = 0.990$ and the magnetic transition with a jump of susceptibility take place at $T_{c1} = 97 \text{ K}$, and another magnetic anomaly occurs at

$T_{c2} = 35$ K, probably corresponding to the antiferromagnetic transition. The HTSE analysis up to eighth order precisely indicates the nearest-neighbour exchange-coupling constant to be $J = 44$ K. The susceptibility behaviour in the cubic phase agrees well with that of the spin-singlet tetramer with $J_{\text{tet}} = 2J$. On the other hand, for the isomorphous compounds MgV_2O_4 and ZnV_2O_4 with $J_{\text{tet}} > T_{c1}$, it is difficult to fit all of the susceptibility data in the cubic phase in the framework of the present tetramer model. Therefore, for the vanadium spinel with $S = 1$, the application of this model is limited to the temperature region above $T \approx J_{\text{tet}}$, and the present bound state may be regarded as *pseudotetramers*. In other words, this restriction may justify the use of an apparently *isolated* tetramer model for the regular spinel B sublattice. In order to understand the magnetic properties of the cubic phase at temperatures below J_{tet} , further theoretical investigations are necessary.

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