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LETTER TO THE EDITOR

A distortion of pseudotetramers coupled with the Jahn–Teller effect in the geometrically frustrated spinel system CdV_2O_4

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Abstract

For the geometrically frustrated spinel system CdV_2O_4 with V^{3+} ($S = 1$) that undergoes structural and magnetic transitions at $T_{c1} = 97$ K, and may exhibit a transition to the antiferromagnetic state at $T_{c2} = 35$ K, the crystal structures at 299 and 85 K have been determined with space groups $Fd\bar{3}m$ and $I4_1/amd$, respectively, by means of x-ray four-circle diffraction. At 85 K, the VO_6 octahedron is distorted due to the Jahn–Teller effect with contraction of the V–O bond along the tetragonal c axis, and the network of V ions is achieved by the linkage of a distorted V_4 -tetrahedron block with two kinds of V–V bonds. On the basis of these structural properties, magnetic susceptibilities at temperatures between T_{c1} and T_{c2} are explained in terms of the tetragonally distorted *pseudotetramer* model.

1. Introduction

Geometrically frustrated spin systems have received a great deal of attention. A state where all of the antiferromagnetic bonds are satisfied at the same time is not allowed and the spin correlation is suppressed, since the elementary unit of the system is the triangle. These properties cause the temperature of the transition to a possible ordered phase to be reduced significantly. A structural phase transition to the lower symmetry sometimes takes place, because there is a gain in orbital and magnetic energies on lifting the degeneracy.

The normal spinel-type $S = 1$ insulator MV_2O_4 , where M is a nonmagnetic divalent ion surrounded tetrahedrally (the so-called A-site) and the trivalent V has an octahedral coordination (the B-site), exhibits the frustration effect [1], since the network of V ions with antiferromagnetic interaction is achieved by the linkage of a regular tetrahedron block that has a V ion at each apex. The compounds with $M = \text{Cd}$ [2], Mg [3] and Zn [4] exhibit the cubic–tetragonal transition due to a Jahn–Teller effect and a jump of magnetic susceptibility at T_{c1} . In addition, at the lower T_{c2} , the temperature dependence of susceptibility shows a kink without a significant change of structure, suggesting the transition to the Néel state, in

which spins are ordered antiferromagnetically in the chain of the tetragonal c plane [5, 6]. Here, T_{c1} and T_{c2} are 97 and 35 K for $M = \text{Cd}$; 64.5 and 45 K for $M = \text{Mg}$; and 52 and 44 K for $M = \text{Zn}$. MgV_2O_4 indicates specific heat anomalies at both temperatures [3]. Using the high-temperature series expansion (HTSE) of up to the eighth order, the Curie constant C and the nearest-neighbour exchange coupling constant J for the cubic phase are estimated as follows: $C = 0.98(2)$, $0.93(3)$ and $0.96(6)$ emu K (mol V) $^{-1}$, and $J = 44(1)$, $92(7)$ and $92(7)$ K for $M = \text{Cd}$, Mg and Zn , respectively [2].

On the basis of the exact solution of the magnetic susceptibility for a set of four interacting spins with J_{tet} for the spinel B sublattice or the pyrochlore lattice, a tetrahedral mean-field (TMF) model was proposed by García-Adeva and Huber [7]. In the MV_2O_4 system, this model was applicable at temperatures above $T \approx J_{\text{tet}}$, where J_{tet} apparently corresponds to $2J$. 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 impossible to account for the data between J_{tet} and T_{c1} [2]. In this sense, the present bound state was regarded as *pseudotetramers*. Recently, a modified theory, referred to as the generalized constant coupling (GCC) approximation, has been proposed [8]. It gives essentially exact results for the susceptibility and specific heat of the classical Heisenberg antiferromagnet on the spinel B sublattice. Mechanisms for lifting the frustration through a coupling between spin and lattice of freedom were also investigated [9–11]. Here, it has been postulated that the V_4 -tetrahedron block for the spinel B sublattice is distorted via a *magnetic* Jahn–Teller effect, leading to a transition from cubic to tetragonal symmetry and the development of bond order in the spin system with unequal spin correlations on different bonds of a tetrahedron. In particular, Tchernyshyov *et al* [10, 11] pointed out that the magnetoelastic couplings may exhibit spin-Peierls phases with bond order but no spin order, and found a range of several possible Néel states.

For the MV_2O_4 system, neither of the analyses for the crystal structure below T_{c1} and the magnetic susceptibility between T_{c1} and T_{c2} have been performed. In this work, the structures of CdV_2O_4 at 299 and 85 K (below T_{c1}) are determined by means of x-ray four-circle diffraction to understand the essence of structural and magnetic anomalies at T_{c1} . Using the exchange coupling constant obtained in the previous work, magnetic susceptibilities above T_{c1} are examined with the GCC for spin-singlet V_4 tetramers that are not isolated but interactive to each other, called *pseudotetramers*. On the basis of the low-temperature structure, the tetragonally distorted pseudotetramer model is considered, and it is applied to the susceptibility data between T_{c1} and T_{c2} . This analysis may reveal the anisotropy of the exchange coupling constant, which basically accounts for the Néel state for the isomorphous compounds MgV_2O_4 and ZnV_2O_4 [5, 6], and may also set limits to the theoretical predictions described above.

2. Crystal structures

The polycrystalline specimens of CdV_2O_4 were first prepared by the solid-state reaction method described in [2]. By heating the mixtures of CdV_2O_4 and 0.1CdO sealed in evacuated silica tubes at 1273 K for one week, small single crystals were obtained, where excess CdO was necessary to compensate for the loss of Cd at high temperatures. The detailed x-ray powder diffraction patterns taken with $\text{Cu K}\alpha$ radiation and θ – 2θ scan method at 300 and 86 K indicated cubic and tetragonal symmetries, respectively, as in [2]. The magnetic susceptibility data for the collected crystals taken with the Faraday method were also in agreement with the previous results. The x-ray four-circle diffraction measurements were performed on a Rigaku AFC-7R diffractometer (custom-made) with graphite-monochromated radiation and the θ – 2θ scan method at temperatures between 85 and 300 K. The single crystals were mounted on a glass

Table 1. The crystal data and parameters used for the structure refinements for CdV₂O₄ at 299 and 85 K. The residual factors R and R_w are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w^2 = \sum w(|F_o| - |F_c|)^2 / \sum wF_o^2$, respectively, where $F_{o(c)}$ is an observed (calculated) structure factor.

	$T = 299$ K	$T = 85$ K
Crystal system	Cubic	Tetragonal
Space group	$Fd\bar{3}m$ (No 227)	$I4_1/amd$ (No 141)
Z	8	4
a (Å)	8.691(1)	6.170(2)
c (Å)	—	8.619(5)
V (Å ³)	656.4(2)	328.1(2)
Radiation; $2\theta_{\max}$ (deg)	Mo $K\alpha$; 90	Mo $K\alpha$; 90
No. of unique reflections; R_{int}	175; 0.040	437; 0.080
No. of observations ($F_o > 3\sigma$)	126	306
Corrections	Lorentz polarization Absorption (0.8436–0.9976) Secondary extinction	Lorentz polarization Absorption (0.7893–1) Secondary extinction
Solution; refinement	Sapi 90 [12]; full-matrix	Sapi 90; full-matrix
No. of variables	9	15
R ; R_w	0.023; 0.025	0.030; 0.038

fibre, and their approximate dimensions were $0.07 \times 0.07 \times 0.07$ mm and $0.04 \times 0.04 \times 0.04$ mm for measurements at 299 and 85 K, respectively. The temperature dependence of the lattice constants on heating indicated the structural transition at $T_{c1} = 97$ K. Below T_{c1} , both single- and powder-diffraction profile widths increased significantly with θ , likely due to the microstrain effect. In order to understand this behaviour precisely, a further study is necessary.

Through the systematic absence of reflections, a statistical analysis of the intensity distribution and the successful solution and refinement of the structure, the crystal data were finally determined as listed in table 1. The space group at 85 K with lattice constant $a_t \simeq a_c/\sqrt{2}$ and $c_t \simeq a_c$, the subscript t(c) meaning tetragonal (cubic), was deduced from detailed considerations of the structure factor F_o map for $(\pm h \pm k l)$ with tetragonal cell constants close to cubic ones ($a_t \simeq a_c$, $c_t \simeq a_c$) on the basis of the criterion of $F_o \geq 3\sigma(F_o)$. A relatively large error in the lattice constant at 85 K may be due to the increase in diffraction profile width as described above. Various parameters for the structure refinements are also summarized. All of the calculations were performed with the teXsan [13] taking the atomic scattering factors from [14] and including anomalous dispersion effects given by [15]¹.

The atomic coordinates, equivalent isotropic thermal parameters and anisotropic displacement parameters at 299 and 85 K are listed in table 2. Selected interatomic distances are listed in table 3. At 299 K, the crystal data and the oxygen u parameter with origin choice at centre ($\bar{3}m$) agree with the previous results [16], and all of the thermal parameters are in a normal range. At 85 K, Cd, V and O atoms are located at positions with Wyckoff letters 4b, 8c and 16h, respectively; the O atom alone has two variable position parameters. Figure 1(a) shows the crystal structure at 85 K projected on the tetragonal c plane. Here, the VO₆ octahedron has four V–O bonds with 2.041 Å in the c plane and two bonds with 2.014 Å along the c axis. Therefore, the d_{xy} -character for the ground-state wavefunction is expected to be enhanced slightly, which may be attributed to the Jahn–Teller effect. The average V–O bond is 2.032 Å, which is equal to the value at 299 K within a standard deviation and is normal for the V³⁺ ion [17]. The network of V ions is expressed by the linkage of a

¹ Supplementary data files are available from the article's abstract page in the online journal; see <http://www.iop.org>.

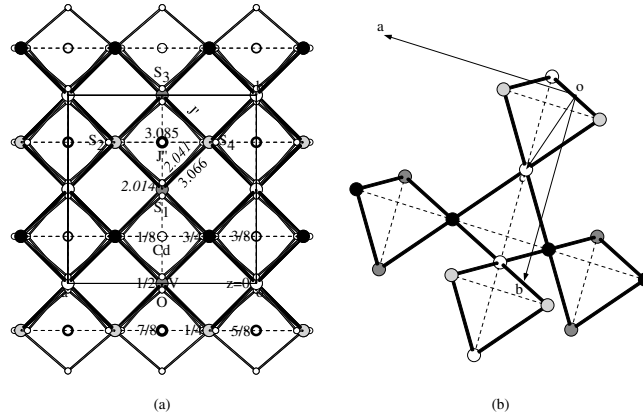


Figure 1. The crystal structure of CdV_2O_4 at 85 K: (a) the projection on the tetragonal c plane, where the numbers attached near the lines indicate V–V (roman) and V–O (italic) bond lengths, and those near the circles show the z coordinates; and (b) the network of V ions achieved by the linkage of a distorted tetrahedron block that has the V ion at each apex. The thick lines and broken lines denote the direct exchange couplings J' and J'' , respectively.

Table 2. Atomic coordinates, equivalent isotropic thermal parameters B_{eq} (\AA^2) and anisotropic displacement parameters U_{ij} of CdV_2O_4 at 299 and 85 K. B_{eq} and U_{ij} are defined by $B_{\text{eq}} = \frac{8}{3}\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha]$ and the parameters are defined in the thermal factor form $T = \exp[-2\pi^2(a^*2U_{11}h^2 + b^*2U_{22}k^2 + c^*2U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$.

	$T = 299$ K			$T = 85$ K		
	Cd	V	O	Cd	V	O
x	$\frac{1}{8}$	$\frac{1}{2}$	0.2672(2)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
y	$\frac{1}{8}$	$\frac{1}{2}$	0.2672	$\frac{1}{4}$	0	−0.0349(4)
z	$\frac{1}{8}$	$\frac{1}{2}$	0.2672	$\frac{1}{8}$	$\frac{1}{2}$	0.2677(3)
B_{eq}	0.503(2)	0.392(2)	0.600(5)	0.450(4)	0.46(1)	0.63(3)
U_{11}	0.0064(1)	0.0050(2)	0.0076(4)	0.0054(1)	0.0059(3)	0.0095(9)
U_{22}	0.0064	0.0050	0.0076	0.0054	0.0055(3)	0.0064(8)
U_{33}	0.0064	0.0050	0.0076	0.0063(2)	0.0063(3)	0.0079(9)
U_{12}	0	−0.0002(1)	−0.0007(4)	0	0	0
U_{13}	0	−0.0002	−0.0007	0	0	0
U_{23}	0	−0.0002	−0.0007	0	−0.0001(2)	0.0016(7)

distorted V_4 tetrahedron block consist of four V–V bonds with 3.066 \AA and two bonds with 3.085 \AA , as shown in figure 1(b). The CdO_4 tetrahedron has equal Cd–O bonds with 2.145 \AA in agreement with the values at 299 K and with those expected from the ionic radius of Cd^{2+} coordinated in a similar manner [17]. The crystals used at 299 and 85 K have the occupancy probabilities for Cd of 0.992(3) and 0.990(5), respectively, indicating that both of them are nearly stoichiometric. While the thermal parameters of Cd become smaller than those at 299 K due to the decrease in thermal vibrations, the values for V and O show inverse behaviours, since the Jahn–Teller effect should increase local distortions in their sites.

Table 3. Selected interatomic distances (Å) and angles (deg) of CdV₂O₄ at 299 and 85 K, where the symmetry operators at 299 K are (1) x, y, z ; (2) $x, \frac{3}{4} - y, \frac{3}{4} - z$; (3) $\frac{3}{4} - x, y, \frac{3}{4} - z$; (4) $\frac{3}{4} - x, \frac{3}{4} - y, z$; (5) $\frac{1}{4} + x, \frac{1}{4} + y, 1 - z$; (6) $\frac{1}{4} + x, 1 - y, \frac{1}{4} + z$; (7) $1 - x, \frac{1}{4} + y, \frac{1}{4} + z$; (8) $x, \frac{5}{4} - y, \frac{5}{4} - z$; (9) $\frac{5}{4} - x, y, \frac{5}{4} - z$; (10) $\frac{5}{4} - x, \frac{5}{4} - y, z$; (11) $x, \frac{1}{4} - y, \frac{1}{4} - z$; (12) $\frac{1}{4} - x, y, \frac{1}{4} - z$; (13) $\frac{1}{4} - x, \frac{1}{4} - y, z$; and those at 85 K are (i) x, y, z ; (ii) $1 - x, -y, 1 - z$; (iii) $\frac{1}{4} - y, \frac{1}{4} - x, \frac{3}{4} - z$; (iv) $\frac{3}{4} + y, \frac{1}{4} - x, \frac{3}{4} - z$; (v) $\frac{1}{4} - y, -\frac{1}{4} + x, \frac{1}{4} + z$; (vi) $\frac{3}{4} + y, -\frac{1}{4} + x, \frac{1}{4} + z$; (vii) $x, \frac{1}{2} - y, z$; (viii) $x, -\frac{1}{2} - y, z$; (ix) $\frac{1}{4} + y, -\frac{3}{4} + x, -\frac{1}{4} + z$; (x) $\frac{3}{4} - y, -\frac{3}{4} + x, -\frac{1}{4} + z$; (xi) $\frac{1}{4} + y, \frac{3}{4} - x, \frac{1}{4} - z$; (xii) $\frac{3}{4} - y, \frac{3}{4} - x, \frac{1}{4} - z$.

$T = 299$ K		$T = 85$ K	
V(1)–O(2, 3, 4, 5, 6, 7)	2.034(1)	V(i)–O(i, ii)	2.014(3)
		V(i)–O(iii, iv, v, vi)	2.041(2)
V(1)–V(2, 3, 4, 8, 9, 10)	3.0726(2)	V(i)–V(vii, viii)	3.085(3)
		V(i)–V(v, vi, ix, x)	3.0662(7)
V(2)–O(1)–V(3, 4),	98.11(8)	V(i)–O(i)–V(ix, x)	98.27(10)
V(3)–O(1)–V(4)		V(ix)–O(i)–V(x)	98.2(1)
Cd(1)–O(1, 11, 12, 13)	2.141(2)	Cd(i)–O(i, vii, xi, xii)	2.145(3)

3. Magnetic properties

The magnetic susceptibilities χ of MV₂O₄ with M = Cd, Mg and Zn for the cubic phase consist of the d-spin term χ_d and the temperature-independent one χ_0 from the Van Vleck and diamagnetic components. Using C and J for the d-spin and χ_0 determined with the HTSE, the reduced spin susceptibilities defined as $\chi_d J/C$ are shown as a function of J/T in figure 2 [2]. The dotted curve and the broken curve indicate results of the HTSE ($\chi^{\text{HTSE}} J/C$) and TMF ($\chi_{\text{tet}} J/C$) with $J_{\text{tet}} = 2J$, respectively, calculated following their expressions given in [2]. According to the GCC [8] without next-nearest-neighbour interaction, the spin susceptibility is given by

$$\chi^{\text{GCC}} = \frac{C}{T} \frac{1 + \epsilon}{1 - \epsilon} \quad (1)$$

where $\epsilon = \chi_{\text{tet}} T/C - 1$. The full curve in figure 2 is drawn with $J_{\text{tet}} = J$ (not $2J$). This model accounts for the data in the cubic phase for CdV₂O₄ with $J < T_{c1}$ as well as those at temperatures above $T \simeq J$ for MgV₂O₄ and ZnV₂O₄ with $J > T_{c1}$, taking account of an error in C (2–6%).

The detailed low-temperature behaviours of the reduced spin susceptibilities as a function of T/J are plotted in figure 3. At first sight, the susceptibility maximum in CdV₂O₄ seems to be explained in terms of the GCC, but there exists a significant difference between the experimental and calculated results, as shown by the broken curve. This indicates that the exchange couplings for the V network change below T_{c1} , and the GCC for the *regular* pseudotetramers should be modified. To understand that difference, let us consider a cluster of four spins on the V₄ unit distorted tetragonally as drawn in figures 1(a) and (b). The Hamiltonian of this cluster is

$$H = J'(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_2 \cdot \mathbf{S}_3 + \mathbf{S}_3 \cdot \mathbf{S}_4 + \mathbf{S}_4 \cdot \mathbf{S}_1) + J''(\mathbf{S}_1 \cdot \mathbf{S}_3 + \mathbf{S}_2 \cdot \mathbf{S}_4) \quad (2)$$

where J' and J'' are the exchange couplings for the thick lines and the broken lines in figures 1(a) and (b), respectively, and \mathbf{S}_i is the spin-1 operator. This Hamiltonian is diagonalized as listed in table 4. While the ground state is a singlet for any antiferromagnetic J' and J'' , the energy level sequence depends on the ratio of J'/J'' ; for example, at $J'/J'' = 5/6$, the spin neutral excitation crosses with the spin triplet excitation. The spin susceptibility for this distorted

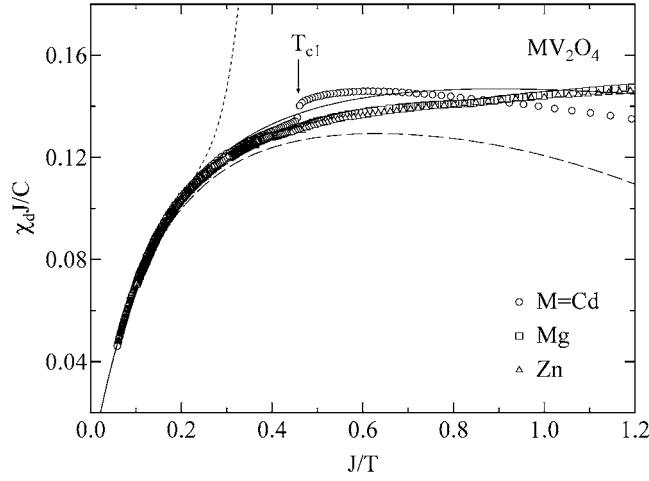


Figure 2. The reduced spin susceptibilities $\chi_d J/C$ as a function of J/T for MV_2O_4 with $M = \text{Cd}$, Mg and Zn , where the full and broken curves indicate fits to the GCC and TMF models, respectively, and the dotted curves denote results calculated in terms of the HTSE.

Table 4. Eigenstates of a tetragonally distorted V_4 tetrahedron cluster with exchange coupling J' and J'' inside the cluster, where S_t is a value of the total spin of the cluster, and G_{S_t} and E_{S_t} are a degeneracy factor and the energy for S_t , respectively.

S_t	G_{S_t}	E_{S_t}	S_t	G_{S_t}	E_{S_t}
4	1	$4J' + 2J''$	1	2	$-3J''$
3	2	$2J'$	1	1	$-J' - 2J''$
	1	$2J''$	2	2	$-3J'$
2	1	$J' - 2J''$	1	1	$-5J' + 2J''$
	2	$-J''$	0	1	$-4J''$
	2	$-J'$	1	1	$-2J' - 2J''$
	1	$-3J' + 2J''$	1	1	$-6J' + 2J''$

pseudotetramer is given by

$$\chi_{dt} = \frac{C}{8T} \frac{\sum_{S_t} G_{S_t} S_t (S_t + 1) (2S_t + 1) \exp(-E_{S_t}/T)}{\sum_{S_t} G_{S_t} (2S_t + 1) \exp(-E_{S_t}/T)} \quad (3)$$

where S_t is a value of the total spin of the cluster, and G_{S_t} and E_{S_t} are a degeneracy factor and the energy for S_t , respectively. The best fit to equation (1) with $\epsilon = \chi_{dt} T/C - 1$ provides $J' = 33.5(2)$ and $J'' = 55.4(1)$ K, when C and χ_0 are fixed at the HTSE values. An agreement between the experimental and calculated results is satisfactory, as indicated by the full curve in figure 3. The values of $J' = 47.4(1)$ and $J'' = 29.3(3)$ K also give a close fit, as shown by the dotted curve, but this is not the case, since the direct exchange couplings along the a and b directions are expected to be more effective due to an enhancement of the d_{xy} character of the ground state. In other words, the V-V spacing dependence of exchange coupling below T_{c1} should differ from that above T_{c1} , where the ground-state wavefunction may not depend significantly on the species of M . The present result explains qualitatively the antiferromagnetic order in the chain of the tetragonal c plane proposed for the isomorphous compounds MgV_2O_4 and ZnV_2O_4 [5, 6]. It is also suggested that the spin-orbit interaction and the Van Vleck component do not change significantly at those temperatures of interest.

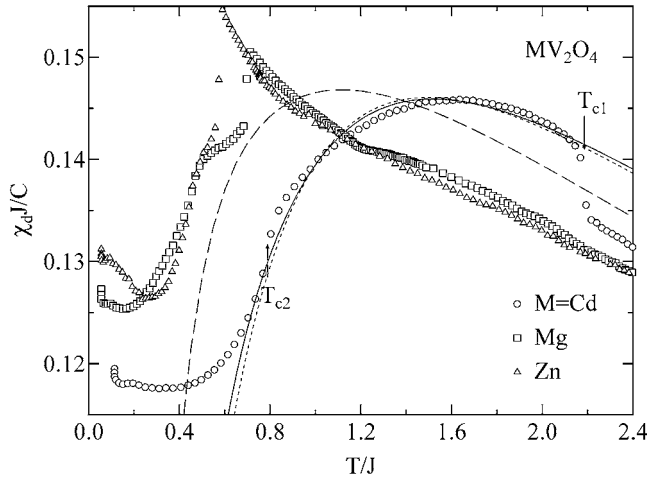


Figure 3. The reduced spin susceptibilities $\chi_d J/C$ as a function of T/J for MV_2O_4 with $M = \text{Cd}$, Mg and Zn , where the full (dotted) curve indicates a fit to the GCC for the tetragonally distorted pseudotetramers with exchange couplings $J' = 33.5$ (47.4) and $J'' = 55.4$ (29.3) K, and the broken curve corresponds to the full curve in figure 2.

Between T_{c1} and J , the behaviours of the reduced spin susceptibilities for MgV_2O_4 and ZnV_2O_4 that are independent of the applied field and the measurement time [3] differ significantly from those calculated for the pseudotetramer with the GCC. It should be noted that $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{V}_2\text{O}_4$ (one of the Zn-Cd solid solution system), in which the $\text{V}^{3+}-\text{V}^{3+}$ interaction is modified randomly to give bond disorder, exhibits a transition to spin-glass-like phases at certain temperature T_g without structural change [18], as in the case of the site-disordered system $\text{Mg}(\text{V}_{1-x}\text{Al}_x)_2\text{O}_4$ [1, 3]. The temperature dependence of the susceptibility between T_{c1} and J is roughly similar to that for $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{V}_2\text{O}_4$ between T_g and J . Therefore, the deviation from the pseudotetramer model at temperatures below J is considered a common nature for the $S = 1$ spinel B sublattice which does not depend significantly on disordered effects.

Below T_{c1} , the frustration for interchains via J' or excited $d_{yz, zx}$ orbital exists, since preliminary measurements of x-ray diffraction below T_{c2} indicate the crystal symmetry to be tetragonal [18]. As introduced before, the mechanisms of transition to the Néel state have been discussed in [10, 11].

4. Conclusions

The crystal structures at 299 and 85 K of CdV_2O_4 that exhibit structural and magnetic transitions at $T_{c1} = 97$ K and the antiferromagnetic transition at $T_{c2} = 35$ K have been determined. The structure at 85 K is tetragonal and the d_{xy} character of the ground state is enhanced due to the usual Jahn–Teller effect, leading to the anisotropy of the exchange coupling constant J . The magnetic susceptibilities for the cubic phase with $J < T_{c1}$ are explained in terms of the GCC with regular pseudotetramers using the same J as determined by the HTSE. The maximum phenomena for the susceptibilities between T_{c1} and T_{c2} (near to J) are also understood by the GCC for the distorted pseudotetramers with two kinds of exchange coupling. While this phase does not have a spin order, it is accompanied by significant modulation of the exchange interaction. It may be unnecessary to invoke the spin-Peierls phase postulated theoretically.

For the isomorphous compounds MgV_2O_4 and ZnV_2O_4 with $J > T_{c1}$, the GCC with regular pseudotetramers accounts for the susceptibility data at $T > J$. However, contrary to the behaviour expected from the GCC, the susceptibility for the cubic phase between J and T_{c1} increases rapidly with decreasing temperature, which does not depend significantly on the disordered effect. Our scenario for CdV_2O_4 presented here seems to be basically effective for the isomorphous compounds, but in order to understand quantitatively the susceptibility anomalies at T_{c1} , detailed theories for $T < J$ are necessary.

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