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Abstract

Vanadium garnets $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$ and $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$ have been successfully synthesized. The X-ray diffraction experiments indicate that these compounds have the garnet structure of cubic symmetry of space group $Ia\bar{3}d$ (O_h^{10}) with the lattice constant of 12.742 Å ($\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$) and 12.666 Å ($\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$), respectively. The magnetic susceptibility of $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$ shows the Curie-Weiss paramagnetic behavior between 4.2 and 350 K. The effective magnetic moment μ_{eff} of $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$ is 3.14 μ_B due to Ni^{2+} ion at A-site and the Weiss constant is -3.67 K (antiferromagnetic sign). For $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$, the simple Curie-Weiss law can not be applicable. The ground state is the spin doublet $^2E(t_2^6e)$ and the first excited state is spin quartet $^4T_1(t_2^5e^2)$, according to Tanabe-Sugano energy diagram on the basis of octahedral crystalline symmetry. This excited spin quartet state just a bit higher than ground state influences strongly the complex temperature dependence of magnetic susceptibility for $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$.

Keywords: A. Inorganic compounds; A. Oxides; B. Chemical synthesis;
D. Magnetic properties

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1. Introduction

The study of garnet compounds has been of great theoretical and experimental interest. The garnet structure has cubic symmetry with space group $Ia\bar{3}d$ (O_h^{10}) as shown in Fig. 1 [1]. The general chemical formula of the oxide garnet may be written as $\{C\}_3[A]_2(D)_3O_{12}$, where C , A , and D -sites are the cation sites. These cation sites are surrounded by oxygen ions O^{2-} at dodecahedron, octahedron, and tetrahedron, respectively. When the D -site is occupied by V^{5+} ion, so called vanadium garnet, many works have been done mainly by Russian researches nearly 30 years ago [2-12], where detailed analysis has not been presented for the magnetic properties.

We have synthesized two vanadium garnets of $NaPb_2Co_2V_3O_{12}$ and $NaPb_2Ni_2V_3O_{12}$ by a solid-state chemical reaction. The synthesis of these compounds has been reported [9]. No physical property has been measured so far. In these compounds of $\{NaPb_2\}[Co_2](V_3)O_{12}$ and $\{NaPb_2\}[Ni_2](V_3)O_{12}$, Na^+ and Pb^{2+} ions occupy C -site, Co^{2+} or Ni^{2+} ions occupy A -site and V^{5+} ions occupy D -site. Here these Co^{2+} and Ni^{2+} ions at A -site are magnetic and the other ions have closed shell with nonmagnetic state.

The magnetic susceptibility of these two garnets, containing magnetic ions in only octahedral A -sublattice with O_h symmetry, has been investigated. The magnetic properties are critically different from an odd and an even number occupation of d -electrons at A -site. The free ions of Co^{2+} ($3d^7$) and Ni^{2+} ($3d^8$) ions have an orbital F state ($L=3$) as ground state. For Co^{2+} ions, there remains Kramer's degeneracy, therefore the correlation between electric field crystalline field and the spin-orbit interaction is more complicated in comparison with Ni^{2+} ion system. This paper will present the difference of the magnetic state between $\{NaPb_2\}[Co_2](V_3)O_{12}$ and $\{NaPb_2\}[Ni_2](V_3)O_{12}$ and will provide detailed discussion.

In the cubic octahedral crystalline field, Ni^{2+} ion has orbital singlet ground state and then, the angular momentum is quenched. For Ni^{2+} ion system, the magnetic moment arises from the spin only value, together with a small orbital contribution through g -value with a little different from 2.0. The Curie-Weiss law can be well applicable for $NaPb_2Ni_2V_3O_{12}$.

On the other hand, Co^{2+} ion in octahedral field has an orbital triplet state, that is, orbital degeneracy. This Co^{2+} ion in octahedral field is of particular interest because the spin and the orbital motion with the spin-orbit interaction contribute to the magnetic moment. Many theoretical studies have been done for Co^{2+} ion in octahedral field, nevertheless the comparison of the theory with the experimental results was qualitative rather than quantitative [13, 14]. The spin Hamiltonian treatment is useful using fictitious spin value [15], but the information is lacking for the excited states. The paramagnetic resonance experimental result gave also the only ground state signal. The Co^{2+} ion in octahedral field has introduced a controversial subject so far because of the difficulties of accurate solution of the Co^{2+} problem.

The magnetic susceptibility result of $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$ is considered for the fairly wide temperature range, which shows the complex temperature dependence. We discuss this result on the basis of the idea that the excited state influences significantly the susceptibility, arising from the presence of a thermally accessible high spin lying above the lower spin ground state. The knowledge of the crystalline electric field enables us to understand the complex temperature dependence of the magnetic susceptibility for $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$, which will be discussed below.

The A-site sublattice forms basically bcc structure. The magnetic ions at A-site are separated by at least two O^{2-} ions. The magnetic interaction is rather novel. As a consequence the theory of superexchange coupling interaction can not be applicable to understand these vanadium systems. The antiferromagnetic ordered state has not been observed down to 4.2 K. The antiferromagnetic Néel order could be below 1 K.

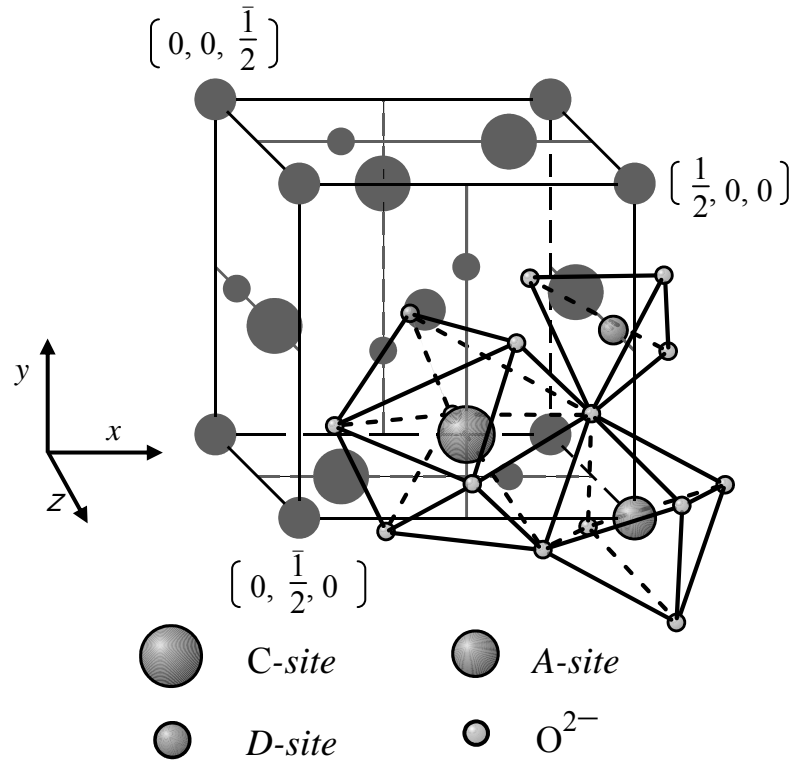
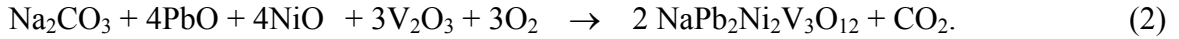
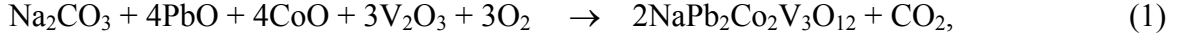


Figure 1. Garnet structure of cubic symmetry of space group $Ia\bar{3}d$ (O_h^{10}). The three different cation sites with the shiny sphere are C-site at $[\frac{1}{4}, \frac{3}{8}, 0]$, A-site at $[\frac{1}{2}, \frac{1}{2}, 0]$ and D-site at $[\frac{1}{2}, \frac{1}{4}, \frac{1}{8}]$.

2. Experimental methods

Powder specimens of $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$ and $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$ were prepared through a solid-state chemical reaction as the same method as previous paper [16], according to the following reactions,



The starting materials, Na_2CO_3 (purity 99.5 %), PbO (99.99 %), V_2O_3 (99.9 %), CoO (99.9 %) and NiO (99.99 %) were mixed in the calculated ratio. Mixed powder materials were put on the alumina boat, and were heated to 1023 K for 24 h in the atmosphere. The crystal structure and the lattice constants were determined by the powder X-ray diffraction method using $\text{CuK}\alpha$ radiation at room temperature. The lattice constant was determined by using the least square methods. The d.c. magnetic susceptibility χ was measured with a Quantum Design superconducting quantum interference device (*rf*-SQUID) magnetometer in the range 4.2 to 350 K at intervals of 5 K in an applied magnetic field 10.000 kOe.

3. Results and discussion

3.1 Powder X-ray diffraction

The polycrystalline specimens of $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$ (color of powder: dark green) and $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$ (yellowish) are successfully synthesized. The powder X-ray diffraction patterns of $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$ and $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$ are shown in Figs. 2 and 3. A small amount of impurity NiO is mixed in $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$. The indices, the comparisons of d spacing between the calculated and the observed values, and observed intensities are listed in Tables 1 and 2. The crystal structure of $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$ and $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$ has cubic symmetry with space group $Ia\bar{3}d$ (O_h^{10}). The lattice constant is evaluated to be 12.742 Å ($\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$) and 12.666 Å ($\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$), respectively.

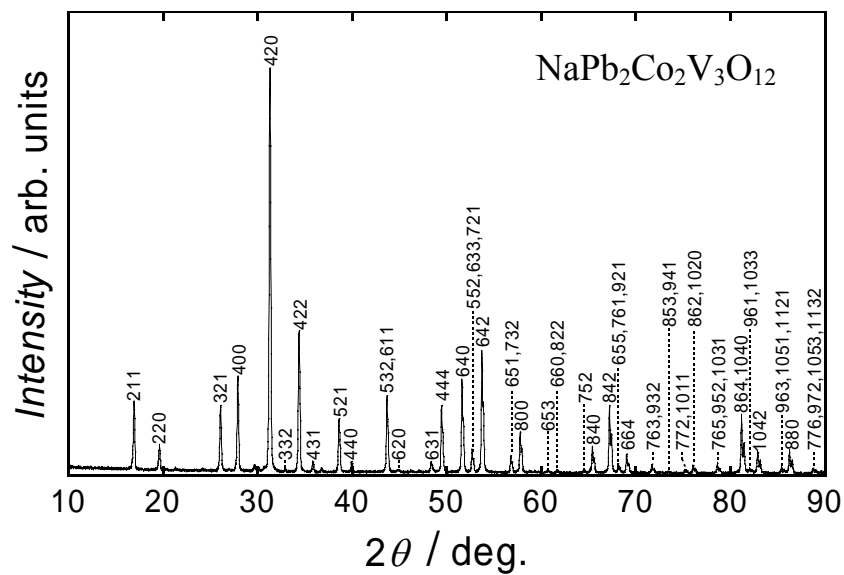


Fig. 2. Powder X-ray diffraction pattern of $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$ at room temperature.

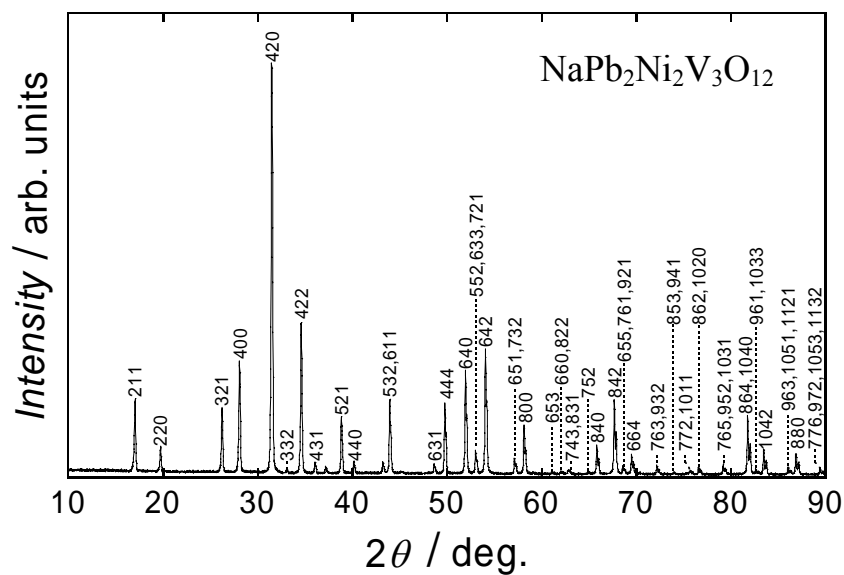


Fig. 3. Powder X-ray diffraction pattern of $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$ at room temperature.

Table 1

Indices, observed and calculated values of d spacings and observed intensities for $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$ with the lattice constant $a = 12.742 \text{ \AA}$

h	k	l	$d_{\text{obs}} / \text{\AA}$	$d_{\text{cal}} / \text{\AA}$	I_{obs}
2	1	1	5.2174	5.2019	15
2	2	0	4.5164	4.505	6
3	2	1	3.4113	3.4054	16
4	0	0	3.1907	3.1855	23
4	2	0	2.8537	2.8492	100
3	3	2	2.7201	2.7166	1
4	2	2	2.6049	2.6009	37
4	3	1	2.5007	2.4989	3
5	2	1	2.3282	2.3264	14
4	4	0	2.2543	2.2525	3
5	3	2	2.0688	2.067	21
6	1	1		2.067	
6	2	0	2.0162	2.0147	1
6	3	1	1.8798	1.8787	3
4	4	4	1.8406	1.8391	20
6	4	0	1.7679	1.767	26
5	5	2	1.7348	1.734	7
6	3	3		1.734	
7	2	1		1.734	
6	4	2	1.7037	1.7027	36
6	5	1	1.619	1.6182	5
7	3	2		1.6182	
8	0	0	1.5933	1.5928	12
6	5	3	1.524	1.523	1
6	6	0	1.5026	1.5017	1
8	2	2		1.5017	
7	5	2	1.4435	1.4427	1
8	4	0	1.4254	1.4246	7
8	4	2	1.3908	1.3903	20
6	5	5	1.3746	1.374	3
7	6	1		1.374	
9	2	1		1.374	
6	6	4	1.3589	1.3583	5
7	6	3	1.3149	1.3142	2
9	3	2		1.3142	
8	5	3	1.2874	1.2871	1
9	4	1		1.2871	
7	7	2	1.2622	1.2616	1
10	1	1		1.2616	
8	6	2	1.25	1.2495	2
10	2	0		1.2495	
7	6	5	1.2154	1.2149	3
9	5	2		1.2149	
10	3	1		1.2149	
8	6	4	1.1834	1.1831	17
10	4	0		1.1831	
9	6	1	1.1734	1.173	1
10	3	3		1.173	
10	4	2	1.1636	1.1632	7
9	6	3	1.1354	1.1351	2
10	5	1		1.1351	
11	2	1		1.1351	
8	8	0	1.1267	1.1262	7
7	7	6	1.1009	1.1007	2
9	7	2		1.1007	
10	5	3		1.1007	
11	3	2		1.1007	

Table 2

Indices, observed and calculated values of d spacings and observed intensities for $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$ with the lattice constant $a = 12.666 \text{ \AA}$

h	k	l	$d_{\text{obs}} / \text{\AA}$	$d_{\text{cal}} / \text{\AA}$	I_{obs}
2	1	1	5.1871	5.1709	15
2	2	0	4.4892	4.4781	5
3	2	1	3.3909	3.3851	15
4	0	0	3.1707	3.1665	26
4	2	0	2.836	2.8322	100
3	3	2	2.7041	2.7004	1
4	2	2	2.5888	2.5854	39
4	3	1	2.4873	2.484	3
5	2	1	2.3144	2.3125	15
4	4	0	2.2414	2.2391	3
5	3	2	2.0562	2.0547	20
6	1	1		2.0547	
6	3	1	1.8689	1.8675	2
4	4	4	1.8295	1.8282	19
6	4	0	1.7578	1.7565	28
5	5	2	1.7251	1.7236	6
6	3	3		1.7236	
7	2	1		1.7236	
6	4	2	1.6938	1.6926	34
6	5	1	1.6097	1.6086	4
7	3	2		1.6086	
8	0	0	1.5843	1.5833	13
6	5	3	1.5145	1.5139	1
6	6	0	1.4938	1.4927	1
8	2	2		1.4927	
7	4	3	1.4768	1.4724	1
8	3	1		1.4724	
7	5	2	1.4348	1.4341	1
8	4	0	1.417	1.4161	8
8	4	2	1.3829	1.382	21
6	5	5	1.3665	1.3658	2
7	6	1		1.3658	
9	2	1		1.3658	
6	6	4	1.3507	1.3502	5
7	6	3	1.307	1.3064	2
9	3	2		1.3064	
8	5	3	1.2799	1.2795	1
9	4	1		1.2795	
7	7	2	1.2548	1.2541	1
10	1	1		1.2541	
8	6	2	1.2428	1.242	2
10	2	0		1.242	
7	6	5	1.2082	1.2077	3
9	5	2		1.2077	
10	3	1		1.2077	
8	6	4	1.1765	1.176	16
10	4	0		1.176	
9	6	1	1.1664	1.166	1
10	3	3		1.166	
10	4	2	1.1568	1.1562	7
9	6	3	1.1288	1.1284	2
10	5	1		1.1284	
11	2	1		1.1284	
8	8	0	1.12	1.1195	6
7	7	6	1.0945	1.0942	2
9	7	2		1.0942	
10	5	3		1.0942	
11	3	2		1.0942	

3.2 Magnetic susceptibility of $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$

Fig. 4 shows the temperature dependence of the magnetic susceptibility of $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$ and $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$. The large increase in the magnetic susceptibility at low temperatures is caused by the isolated localized magnetic moment of Co^{2+} or Ni^{2+} ion. The inverse magnetic susceptibilities are indicated in Fig. 5. The susceptibility of $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$ over the temperature range 4.2 to 350 K are well described by a modified Curie-Weiss law,

$$\chi = \chi_0 + \frac{C}{(T - \theta)} \quad , \quad (3)$$

where χ_0 is the temperature independent term, C the Curie constant, T the temperature and θ the Weiss constant. For $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$ at the temperature range 4.2 to 350 K, the experimental results are $\chi_0 = 7.10 \times 10^{-4} \text{ emu mol-f.u.}^{-1}$ which includes experimental errors, $C = 2.46 \text{ K emu mol-f.u.}^{-1}$ and $\theta = -3.67 \text{ K}$. The amount of diamagnetic contribution caused by the atomic core orbital electrons is evaluated to be $\chi_{\text{dia}} = -2.39 \times 10^{-4} \text{ emu mol-f.u.}^{-1}$ [17]. The value of effective magnetic moment, $\mu_{\text{eff}} = g\sqrt{S(S+1)}$ in the unit of Bohr magneton μ_B , is extracted to be $3.14 \mu_B$ from the Curie constant C , which is close to the spin only value 2.83 expected for $S = 1$ of Ni^{2+} , where the Lande's g -factor may be 2.2.

The electron configuration d^8 for Ni^{2+} in the cubic field with octahedral symmetry does not cause the transition from high- to low spin state when the crystalline field strength parameter Dq varies from weak to strong. The ground state of d^8 for Ni^{2+} in the cubic field maintains the spin triplet state ${}^3A_2(t_2^6 e^2)$ with any changing the value of Dq , furthermore, the excited states of the energy levels in the cubic field are rather higher than that of the ground state. Therefore the spin triplet state is well defined. This situation guarantees quenching of the orbital angular momentum and then assures the applicability of the Curie-Weiss law to the susceptibility data of $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$. Consequently, all the experimental results give the reasonable magnitudes expected.

3.3 Magnetic susceptibility of $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$

The susceptibility result of $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$ leads to the absolutely different situation from the $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$. Fig. 5 indicates that the susceptibility of $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$ does not fit well the Curie-Weiss law over the temperature range of 4.2 to 350 K. If we assume the Curie-Weiss law for the higher temperature region 100 to 350 K, the experimental results give the values of $\chi_0 = -4.79 \times 10^{-3} \text{ emu mol-f.u.}^{-1}$, $C = 9.96 \text{ K emu mol-f.u.}^{-1}$ and $\theta = -73.1 \text{ K}$. The evaluated value of χ_{dia} is $-2.41 \times 10^{-4} \text{ emu mol-f.u.}^{-1}$ [17], and μ_{eff} is extracted to be $6.31 \mu_B$ which is much higher than that of the spin only value 3.87 expected for $S = 3/2$ of Co^{2+} . In addition, the magnitude of the antiferromagnetic Weiss temperature θ is too high because of the no sign of magnetic ordered state down to 4.2 K. On the other

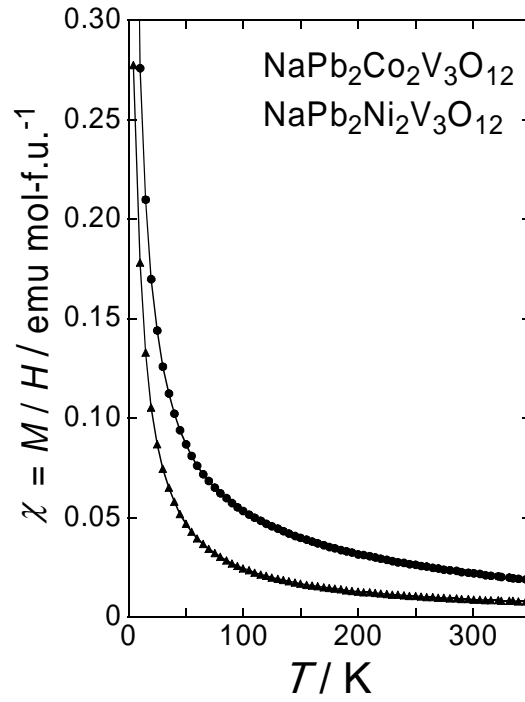


Fig. 4. Magnetic susceptibility of $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$ and $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$ as a function of temperature in a constant magnetic field of 10.000 kOe.

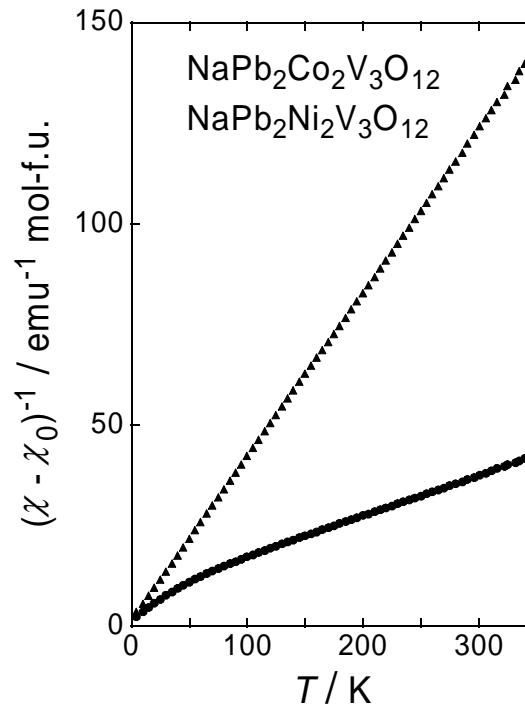


Fig. 5. The inverse magnetic susceptibility of $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$ and $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$, here the value of χ_0 is different between two lines.

hand, at lower temperature region over 10 to 60 K, the experimental results of $\chi_0 = 1.89 \times 10^{-2}$ emu mol-f.u.⁻¹, $C = 3.68$ K emu mol-f.u.⁻¹ and $\theta = -4.36$ K are obtained. The effective magnetic moment μ_{eff} is $3.84 \mu_B$; this value is fairly close to the spin only value $3.87 \mu_B$ expected for $S = 3/2$.

At first sight, these experimental results for the susceptibility of NaPb₂Co₂V₃O₁₂ may lead to an apparent interpretation that the high- and low spin crossover takes place approximately 100 K where in the higher temperature μ_{eff} is $6.31 \mu_B$ while $3.84 \mu_B$ in the lower temperature. However, it should be noted that these values of the effective magnetic moment μ_{eff} are completely different from these magnitudes expected for $3.87 \mu_B$ ($S = 3/2$ high spin state) and for $1.73 \mu_B$ ($S = 1/2$ low spin state). Consequently this simple interpretation is wrong. The authors would like to point out careful understanding and discussion as follows.

The unified physical picture has been derived from the outstanding Tanabe-Sugano diagram based on the cubic crystalline electric field theory with the octahedral symmetry [18, 19]. Here we present the significant energy levels only around ground state as shown in Fig. 6, which refers to the Tanabe-Sugano diagram of ref. 18. The crystalline field parameter Dq indicates the strength of the crystalline field and B is Racah's parameter defined as the value of linear combination of Slater integrals introduced by Racah [18,19]. The transition from the weak crystalline field with high spin state to the strong crystalline field with low spin state takes place for Co²⁺ ion at the vertical line of $Dq/B \sim 2.17$. Unfortunately the Rietveld refinement has not been done for NaPb₂Co₂V₃O₁₂, while the Rietveld analysis has been accomplished for a prototype garnet of AgCa₂Co₂V₃O₁₂ [20]. The result of AgCa₂Co₂V₃O₁₂ tells interesting result that the CoO₆-octahedron is firm and tight. The bond length between Co²⁺ and O²⁻ is 2.087 Å, which is extremely short and sufficient to provide the strong crystalline field. Presumably the same strong crystalline field takes place in the NaPb₂Co₂V₃O₁₂.

Our experimental results may indicate that the value of Dq of NaPb₂Co₂V₃O₁₂ is located at the just after the transition of from high spin to low spin state. Here Dq/B is ~ 2.3 just a little larger than $Dq/B \sim 2.17$. This Tanabe-Sugano diagram for d^7 configuration for Co²⁺ at $Dq/B \sim 2.3$ indicates that the energy level constructs from the ground state ${}^2E(t_2^6 e)$ at the bottom to ${}^4T_1(t_2^5 e^2)$, 2T_1 , 2T_2 , ${}^2T_2(t_2^4 e^3)$, 4T_1 , 2A_1 , ${}^4A_2(t_2^3 e^4)$, and the highest level of 2A_2 . On the other hand, the energy levels for the free ion of Co²⁺ with $Dq/B = 0$ from the bottom ground state to the highest state are 4F , 4P , 2G , 2H , 2P , 2D_a , 2F , and 2D_b . In the influence of the cubic crystalline field, 4F ground level splits into ${}^4T_1(t_2^5 e^2)$, ${}^4T_2(t_2^4 e^3)$ and ${}^4A_2(t_2^3 e^4)$ and the second excited state 2G plays an important role because 2G state also splits under the influence of the cubic crystalline field. One of the split component of 2G state is 2E state which becomes the ground state in the strong crystalline field of value Dq/B larger than ~ 2.17 . This 2E state crosses all the quartet levels on its way down, as can be seen in the Tanabe-Sugano diagram, see Fig. 6.

The magnitude of $Dq/B \sim 2.3$ for NaPb₂Co₂V₃O₁₂ gives two significant levels of the ground state ${}^2E(t_2^6 e)$ and the first excited state of ${}^4T_1(t_2^5 e^2)$. The ${}^4T_1(t_2^5 e^2)$ level is extremely

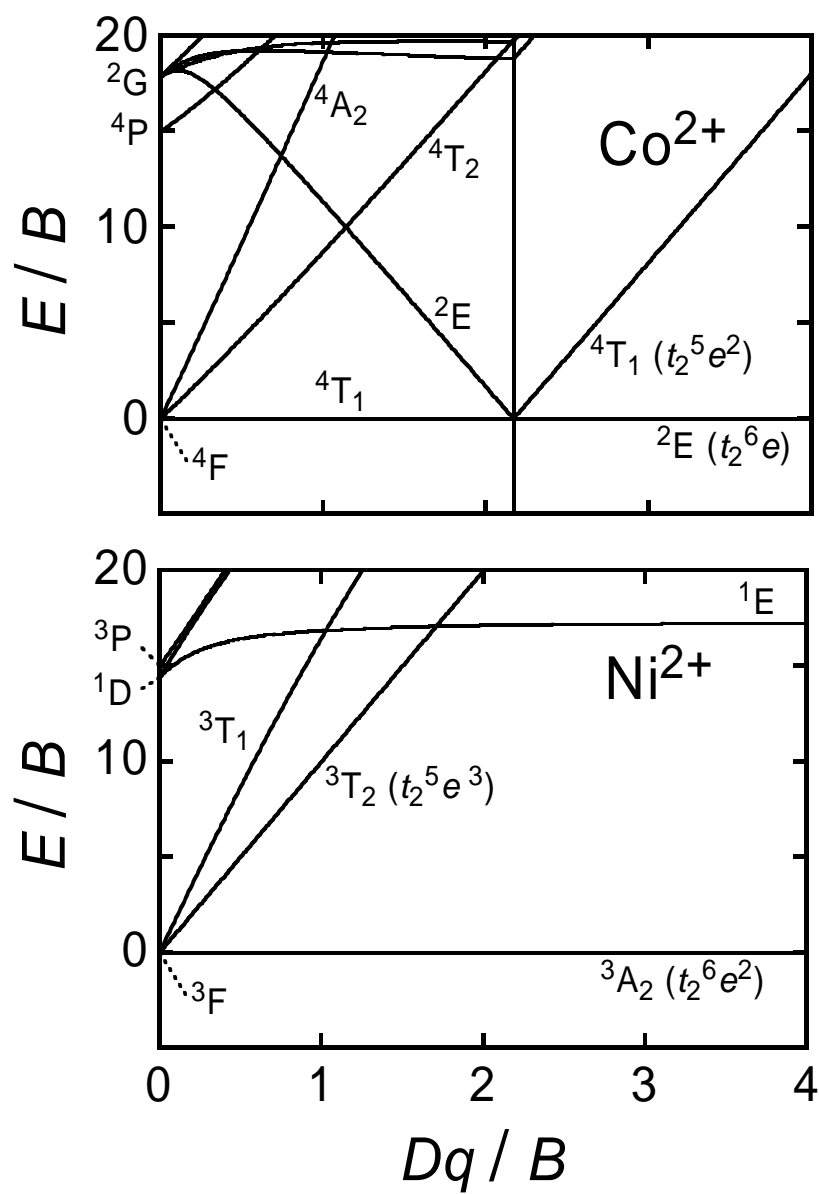


Fig. 6. The energy diagram close to the ground state which is referred to as the Tanabe-Sugano diagram based on the cubic crystalline electric field theory with the octahedral symmetry. The level energy (ordinate) is measured from the ground state and the strength of the crystalline field (abscissa) is scaled by B as unit, see text and ref. 16.

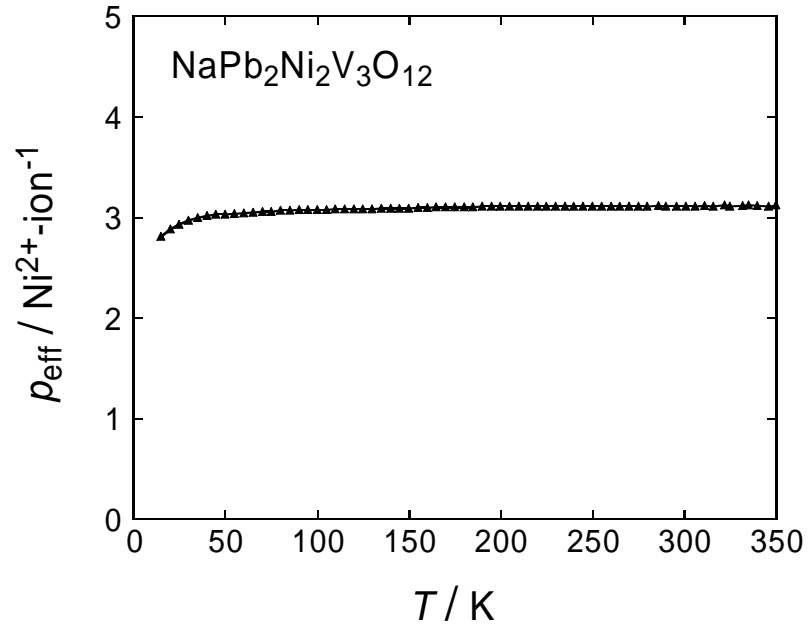


Fig. 7. Temperature dependence of p_{eff} for $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$.

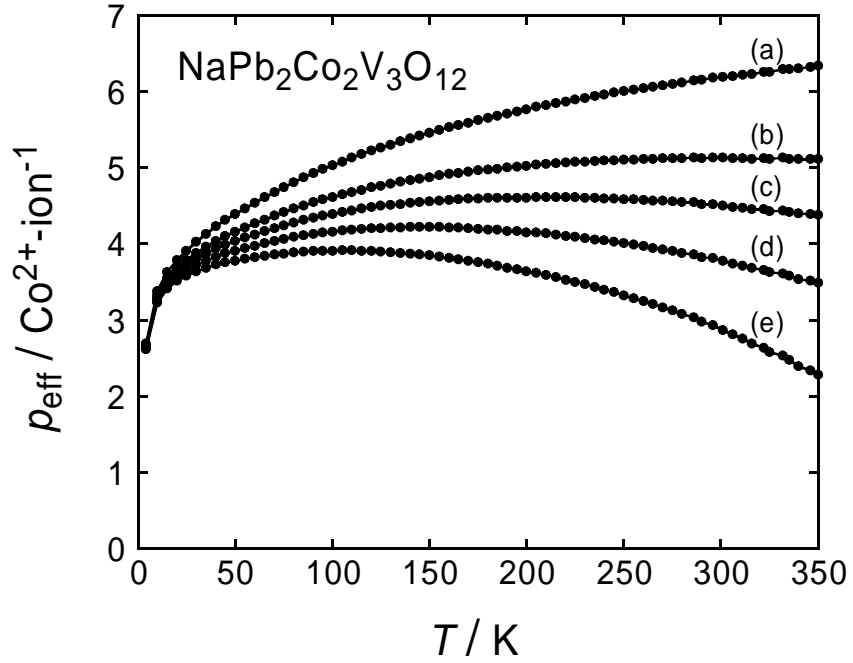


Fig. 8. The χ_0 dependence on p_{eff} of $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$ as a function of temperature: (a) $\chi_0 = -0.010$ emu mol-f.u.⁻¹, (b) 0.000, (c) 0.005, (d) 0.010 and (e) 0.015, here these values of χ_0 include appreciable experimental errors.

close to ${}^2E(t_2^6e)$ and a little higher than that. We can not neglect the thermally accessible occupation of the excited state of ${}^4T_1(t_2^5e^2)$ for the interpretation of the magnetic susceptibility.

Here let us take a next step. It is unable for us to pursue a quantitative analysis of the susceptibility because of the many unknown parameters in the crystalline field theory. Therefore we try a feasible approach where the basic view point from the Tanabe-Sugano diagram is maintained. We introduce an effective magnetic moment p_{eff} which is expressed by [21],

$$p_{\text{eff}} = \sqrt{\frac{3k_B T \chi}{N}} \quad , \quad (4)$$

here χ is the experimental value of temperature dependent magnetic susceptibility, T temperature, k_B the Boltzmann's constant and N the number of ion. Temperature dependence of p_{eff} is shown in Figs. 7 and 8. Fig.7 indicates the same values of $\chi(T)$ as these obtained in Figs. 4 and 5 for a comparison. The straight and horizontal line is seen over the wide temperature range over 50 to 300 K in $\text{NaPb}_2\text{Ni}_2\text{V}_3\text{O}_{12}$, which supports the applicability of the Curie-Weiss law. Nevertheless, $\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$ demonstrates the curved line for p_{eff} as seen in Fig. 8. We note that the measured value of $\chi(T)$ includes the temperature independent Van Vleck paramagnetic contribution in addition to the stated diamagnetic core contribution χ_0 and/or appreciable experimental errors, then we must subtract before being compared with theoretical results. Fig. 8 shows the χ_0 dependence on p_{eff} as a function of temperature. Any magnitude of χ_0 does not fulfill and reproduce a straight and horizontal line. The complex temperature dependence of the susceptibility is reflected in the performance of p_{eff} , which originates from the existence of the first excited spin quartet ${}^4T_1(t_2^5e^2)$ state just a bit higher than the ground spin doublet ${}^2E(t_2^6e)$ state. Consequently two magnetic states with $S=3/2$ and $S=1/2$ are excited and active magnetically at higher temperature. Each curve converges on the low spin state of $S = 1/2$ at lowest temperature, as seen in Fig. 8. It should be noticed that our model does not mean the simple high($S=3/2$) to low spin state($S=1/2$) transition, but the z-component S_z of spin is 6, because $+1/2, -1/2$ from ground state and $+3/2, +1/2, -1/2$, and $-3/2$, so that this value corresponds effectively (not exactly) to $S=5/2$ where the presence of a thermally accessible spin $3/2$ excited. The above analysis is treated within the framework of the Tanabe-Sugano theory.

It should be noted, nevertheless, that the spin-orbit coupling effect has been neglected in this theory. Low [13] has given us another nice route to reach the Co^{2+} problem in the octahedral field on the basis of the spin-orbit coupling. The orbital degeneracy is not removed because of the Kramer's degeneracy. The energy separation between the ground state and the first excited state is estimated approximately to be 400 cm^{-1} (580 K) in this theory, see ref. [13]. This value is too high to understand our experimental results of the temperature dependence of the susceptibility, therefore this situation is not realistic in

$\text{NaPb}_2\text{Co}_2\text{V}_3\text{O}_{12}$. The spin Hamiltonian method is also useful using fictitious spin value with rather complicated g -factor [15], but information is lacking for the excited states. The paramagnetic resonance experimental result EPR gave also the only ground state signal. Only one fictitious spin in the ground state can not account for our results, consequently our result suggests that one fictitious spin is not realistic to understand the susceptibility over the wide temperature range.

Finally, we would like to point out that many previous researchers experienced a severe struggle for understanding the magnetic susceptibility for the almost same structure of $\text{NaCa}_2\text{Co}_2\text{V}_3\text{O}_{12}$. If the incorrect energy levels are introduced, then unphysical interpretation has been given unfortunately. For example of $\text{NaCa}_2\text{Co}_2\text{V}_3\text{O}_{12}$ [3], the spin value for magnetic study [10], and the difficulty of interpretation in the absorption spectrum [5]. These difficulty can be removed by the existence of excited spin quartet state $^4T_1(t_2^5 e^2)$ just a little bit higher than ground spin doublet state $^2E(t_2^6 e)$ state, on the basis of crystalline field theory.

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