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Magnetic properties of ordered perovskite oxide $Ba_3ZnU_2O_9$

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Abstract

Uranium complex oxide with the ordered perovskite structure, $Ba_3ZnU_2O_9$ was prepared, and its magnetic susceptibility measured between 4.2 K and room temperature. No magnetic cooperative phenomenon was found down to 4.2 K. The effective magnetic moment of uranium is 0.57 μ_B. The crystal field parameters and orbital reduction factors for this compound are determined from the analysis of the optical spectrum published previously. The effective moment and temperature independent paramagnetic susceptibility are calculated and compared with the experimental results.

Keywords: Uranium; Ordered perovskite; Oxides; Magnetic properties; Magnetic susceptibility

1. Introduction

The magnetic and optical properties of actinides are characterized by the behavior of 5f electrons. For the 5f compounds, the crystal field, spin–orbit coupling, and electron–electron repulsion interactions are of comparable magnitude, which makes the analysis of the experimental results complicated. However, in the case of actinide ions having the $[Rn]5f^1$ electronic configuration, such as a U^{5+} ion, the situation is considerably simplified because there are no electronic repulsion interactions. Therefore, the theoretical treatments of such ions is easier and we may obtain a deeper understanding of the behavior of 5f electrons in solids.

Among many uranium complex oxides, the "ordered perovskites" based on the $BaUO_3$ attract our attention. Replacing half of the uranium ions with trivalent rare earth ions forms the ordered perovskites Ba_2MUO_6, oxidizing the rest of the uranium ions to the pentavalent state [1–4]. Fig. 1 shows the simple perovskite, ideal $BaUO_3$, and the ordered perovskite Ba_2MUO_6 in which M and U order. In these perovskites, both M and U are coordinated by six oxygens forming regular octahedra. This high coordination symmetry around the U^{5+} ion in addition to the f^1 configuration enables us to analyze the experimental results more easily. We have already reported the magnetic properties of Ba_2MUO_6 (M = Sc,Y,Gd,Yb) [5].

Our attention is now focused on the ordered perovskites with the general formula $Ba_3M^{2+}U_2^{5+}O_9$ (M^{2+} = alkaline earth ion), i.e. replacing one-third of the uranium ions with divalent metal ions also forms ordered perovskite and oxidizes the rest of the uranium ions to the pentavalent state [6]. This formula should be written as $Ba_2(M_{2/3}U_{1/3})UO_6$.

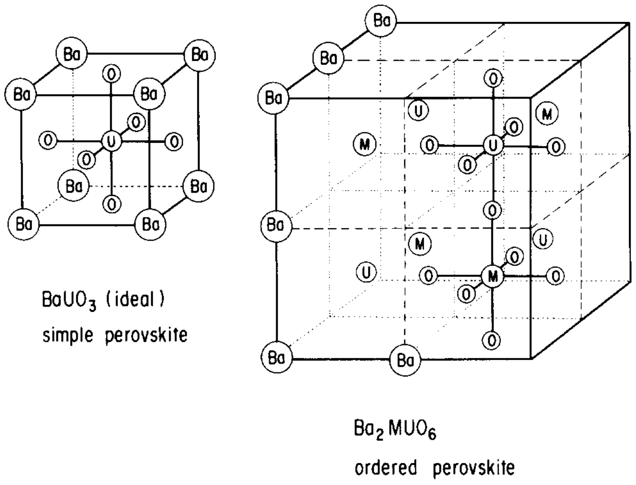

Fig. 1. Simple (left) and "ordered" (right) perovskite structures.

Magnetic measurements are effectively used to elucidate the electronic states of the uranium and M ions in these ordered perovskites, Ba_2MUO_6 and $Ba_3MU_2O_9$. Since the oxygen stoichiometric $BaUO_3$ shows temperature-independent paramagnetism over a wide temperature range [7] and since hexavalent uranium ion is diamagnetic, the magnetic behavior of U^{5+} in the Ba_2MUO_6 and $Ba_3MU_2O_9$ is quite different from those of U^{4+} and U^{6+}.

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In a preceding paper [8] we reported the formation of two ordered perovskites, $Ba_3CaU_2O_9$ and $Ba_3SrU_2O_9$, and their magnetic properties. Although the magnetic behavior of these compounds was expected to be similar to their optical reflectance spectra [6], the temperature dependence of the magnetic susceptibilities between them is different. One reason for this is the oxygen nonstoichiometry found in these compounds, especially the oxygen deficiency found in the $Ba_3CaU_2O_9$.

In this study, we tried to prepare the oxygen stoichiometric $Ba_3ZnU_2O_9$, and measured its magnetic susceptibility in the temperature range between 4.2 K and room temperature to elucidate the electronic state of U^{5+} ion in the crystal. The crystal field parameters and orbital reduction factors for this compound are determined on the basis of the octahedral crystal field model.

2. Experimental details

2.1. Sample preparation

$Ba_3ZnU_2O_9$ was prepared by the following reactions:

$$U_3O_8+3ZnO+6BaCO_3 \xrightarrow{\text{in air}} 3Ba_2ZnUO_6 \quad (1)$$

$$Ba_2ZnUO_6+BaUO_3 \xrightarrow{\text{in vacuo}} Ba_3ZnU_2O_9 \quad (2)$$

As the starting materials, $BaCO_3$, ZnO, and U_3O_8 were used. Before use, $BaCO_3$ was heated in air at 800 °C to remove any moisture, and U_3O_8 was oxidized in air at 850 °C to form the stoichiometric compound.

To prepare Ba_2ZnUO_6, the $BaCO_3$, ZnO, and U_3O_8 were weighed in the intended stoichiometric metal ratio, Ba:Zn:U = 2:1:1. After being finely ground in an agate mortar, the mixtures were pressed into pellets and then heated in air at 1000 °C for 150 h. This grinding, mixing, and heating procedure was repeated to prepare a good crystalline specimen.

The $BaUO_3$ was prepared by the following reactions:

$$3BaCO_3+U_3O_8 \xrightarrow{\text{in air}} 3BaUO_4 \quad (3)$$

$$BaUO_4+H_2 \xrightarrow{\text{H}_2\text{ flow}} BaUO_3+H_2O \quad (4)$$

To reduce $BaUO_4$ to $BaUO_3$, it was heated in a flow of H_2 gas at 1300 °C for a day.

The $Ba_3ZnU_2O_9$ was prepared by heating mixtures of Ba_2ZnUO_6 and $BaUO_3$ in an evacuated quartz tube at 1000 °C for 150 h. To avoid the reaction of the mixtures with quartz, the mixtures were wrapped with molybdenum foil. After being cooled to room temperature, the sample was crushed into powder, pressed into pellets, and reacted once more under the same conditions.

2.2. Analysis

2.2.1. X-ray diffraction analysis

The X-ray diffraction analysis was performed with CuKα radiation on a Philips PW 1390 diffractometer equipped with a curved graphite monochromator. The lattice parameter of the sample was determined by a least-squares method.

2.2.2. Determination of the oxygen content

The oxygen nonstoichiometry in the sample was checked by the back-titration method [9,10]. A weighed amount of the sample was dissolved in excess cerium(IV) sulfate solution, which had been standardized in advance with stoichiometric UO_2. Then the excess cerium(IV) was titrated against a standard iron(II) ammonium sulfate solution with the ferroin indicator. The oxygen amount was evaluated for a predetermined Ba:Zn:U ratio.

2.3. Magnetic susceptibility measurement

The magnetic susceptibility was measured with a Faraday-type torsion balance. The temperature range of the susceptibility measurements was between 4.2 K and room temperature. The apparatus was calibrated with a $CoHg(SCN)_4$ as a standard [11]. The temperature of the sample was measured by a "normal" Ag vs. Au-0.07 at.%Fe thermocouple (4.2 K ~ 40 K) [12] and an Au–Co vs. Cu thermocouple (10 K ~ room temperature). To examine the field dependence at 4.2 K, 77.3 K, and room temperature, the magnetic susceptibility was measured in each of the field strengths of 2800, 4700, 6900, 9000, and 10 600 G. Details of the experimental procedure have been described elsewhere [13].

3. Results and discussion

The X-ray diffraction analysis shows that the specimen prepared in this study has a cubic ordered perovskite structure. The lattice parameter is 8.4833 Å. From the chemical analysis of the oxygen content, it is $Ba_3ZnU_2O_{8.99}$. This result indicates that, in view of the error limits for this analysis, the prepared specimen is considered to be entirely ideally stoichiometric, i.e. we have succeeded in preparing the oxygen stoichiometric $Ba_3ZnU_2O_9$ in the evacuated quartz tube.

Fig. 2 shows the variation of the reciprocal magnetic susceptibility with temperature for $Ba_3ZnU_2O_9$, which was measured in a magnetic field of 9000G. From the susceptibility measurements at various magnetic fields, the susceptibility of $Ba_3ZnU_2O_9$ is found to be independent of the magnetic field strength even at 4.2 K. With decreasing temperature, the susceptibility increases; no magnetic cooperative phenomenon is found

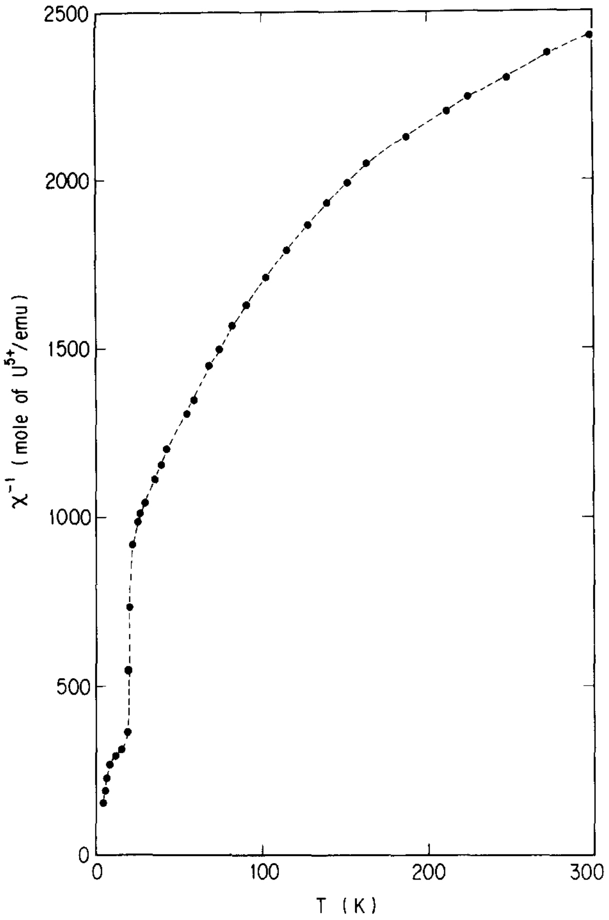

Fig. 2. Temperature dependence of reciprocal magnetic susceptibility of $Ba_3ZnU_2O_9$.

down to 4.2 K. This temperature dependence of the susceptibility is similar to that found for $Ba_3SrU_2O_9$ [8]. The susceptibility of $Ba_3ZnU_2O_9$ increases rapidly when the temperature is decreased through ca. 20 K. This behavior is reproducible.

Fig. 2 also clearly indicates that the possibility of oxidation species $Ba_3Zn^{2+}U^{4+}U^{6+}O_9$ should be excluded. In that case its magnetic property is expected to be similar to that of the oxygen-stoichiometric $BaUO_3$ (temperature-dependent paramagnetism) [7], because the U^{4+} ion in an octahedral crystal field is the only paramagnetic ion in this solid. However, the experimental results (Fig. 2) show that the susceptibility of $Ba_3ZnU_2O_9$ varies with temperature and that it does not follow a simple Curie–Weiss law. By extrapolating the reciprocal temperature $1/T$ to zero for the susceptibility vs. reciprocal temperature curve, we obtain the temperature-independent paramagnetic susceptibility 290×10^{-6} emu/mol. Then, the susceptibility of $Ba_3ZnU_2O_9$ measured in this study may be represented by the equation $\chi = 0.0405/(T+32.4) + 290 \times 10^{-6}$ emu/mol. The effective magnetic moment of uranium in this $Ba_3ZnU_2O_9$ is calculated to be 0.57 μ_B from the temperature dependent part of the susceptibility. This value is much smaller than that for the moment calculated for a free f^1 ion, U^{5+} (2.54 μ_B), which indicates that the crystal field effect on the magnetic property of an f electron is large.

Since the optical reflectance spectrum is available for this compound [14], we can determine the crystal field energy levels. Then, we can calculate the magnetic susceptibility and evaluate the effective magnetic moment of uranium.

In this compound, the U^{5+} ions are in the octahedral crystal field by six oxygen ions. Fig. 3 shows the effects of perturbing the f^1 orbital energy levels successively by an octahedral field and spin-orbit coupling. In an octahedral crystal field, the seven-fold degenerate energy state of the f orbitals is split into Γ_2, Γ_5, and Γ_4 states, where Δ and Θ represent the parameters of the crystal field strengths. If spin–orbit coupling is taken into

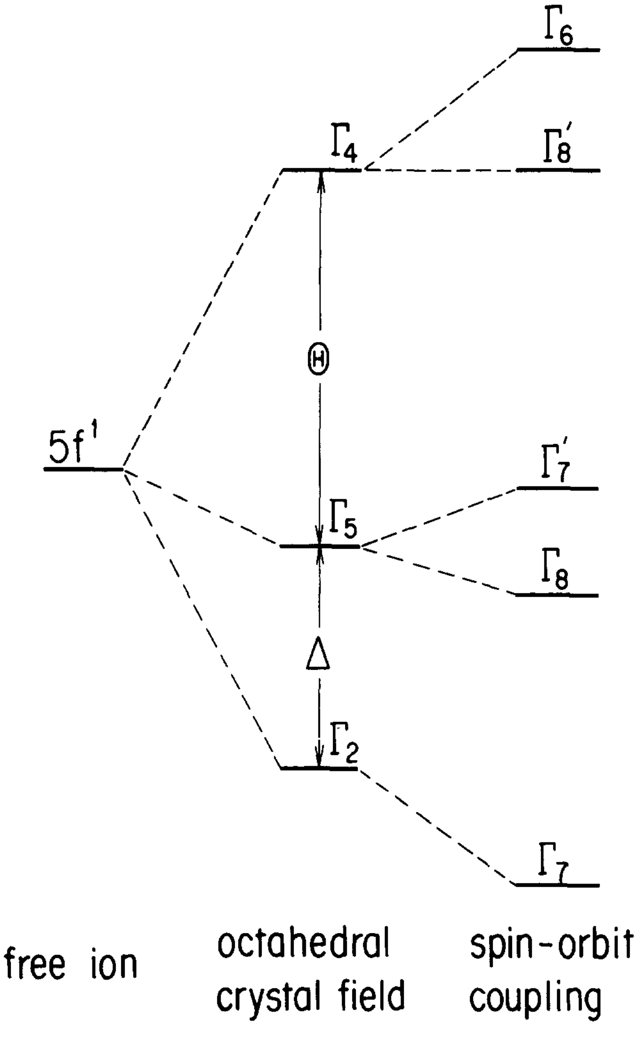

Fig. 3. f^1 orbital splitting perturbed by octahedral crystal field and spin–orbit coupling.

account, the Γ_2 orbital state is transformed into Γ_7, whereas the Γ_5 and Γ_4 states are split into Γ_7^* and Γ_8, and Γ_6 and Γ_8^*, respectively. The ground state Kramers doublet is the Γ_7 state and is coupled to the excited Γ_7^* state arising from the Γ_5 orbital, by the spin–orbit coupling. The Γ_8 state arising from the Γ_5 orbital state is also coupled to the Γ_8^* state arising from the Γ_4 orbital state by the same spin–orbit coupling interaction. The energy matrices for the Γ_7, Γ_8, and Γ_6 states are:

$$\Gamma_7\colon \begin{vmatrix} 0 & \sqrt{3k}\zeta \\ \sqrt{3k}\zeta & \Delta-\tfrac{1}{2}k\zeta \end{vmatrix}$$

$$\Gamma_8\colon \begin{vmatrix} \Delta+\tfrac{1}{4}k\zeta & \tfrac{3}{4}\sqrt{5kk'}\zeta \\ \tfrac{3}{4}\sqrt{5kk'}\zeta & \Delta+\Theta-\tfrac{3}{4}k'\zeta \end{vmatrix} \qquad (5)$$

$$\Gamma_6\colon |\Delta+\Theta+\tfrac{3}{2}k'\zeta|$$

Here ζ is the spin–orbit coupling constant and k and k' are the orbital reduction factors for an electron in a Γ_5 orbital state and Γ_4 orbital state, respectively [15]. Diagonalization of the energy matrix produces the ground state Γ_7 and the excited state Γ'_7, and the corresponding wavefunctions are written as follows:

$$\begin{aligned} |\Gamma_7\rangle &= \cos\theta\,|{}^2F_{5/2}, \Gamma_7\rangle - \sin\theta\,|{}^2F_{7/2}, \Gamma_7^*\rangle \\ |\Gamma'_7\rangle &= \sin\theta\,|{}^2F_{5/2}, \Gamma_7\rangle + \cos\theta\,|{}^2F_{7/2}, \Gamma_7^*\rangle \end{aligned} \qquad (6)$$

where θ is the parameter describing the admixture of the Γ_7 levels in the ground state with the relation

$$\tan 2\theta = \frac{2\sqrt{3k}\zeta}{\Delta-\tfrac{1}{2}k\zeta} \qquad (7)$$

The g value for the ground Γ_7 doublet is calculated as follows:

$$\begin{aligned} g &= 2\langle\Gamma_7 L+2S|\Gamma_7\rangle \\ &= 2\cos^2\theta - 4\sqrt{k_3}\sin 2\theta - \tfrac{2}{3}(1-k)\sin^2\theta \end{aligned} \qquad (8)$$

This g value is experimentally determined by the electron paramagnetic resonance (EPR) spectrum measurements. In this study, we tried to measure the EPR spectrum for $Ba_3ZnU_2O_9$. However, no EPR spectrum was measured even at 4.2 K. As will be described later, the g value for the ground Γ_7 doublet is also determined for the temperature-dependent part of the susceptibility. The energies for the Γ_7, Γ_8, Γ'_7, Γ'_8, and Γ_6 (in the order of ascending energies) are

$$\begin{aligned} E(\Gamma_7) &= \Delta-\tfrac{1}{2}\{k+2\sqrt{3k}\cot\theta\}\xi \\ E(\Gamma_8) &= \Delta+\Theta-\tfrac{3}{4}\{k'+\sqrt{5kk'}\cot\varphi\}\zeta \\ E(\Gamma'_7) &= \sqrt{3k}\cot\theta\zeta \\ E(\Gamma'_8) &= \Delta+\tfrac{1}{4}\{k+3\sqrt{5kk'}\cot\varphi\}\zeta \\ E(\Gamma_6) &= \Delta+\Theta+\tfrac{3}{2}k'\zeta \end{aligned} \qquad (9)$$

where φ is the parameter describing the admixture of the Γ_8 levels in the excited state.

Since the effective magnetic moment of U^{5+} ion is obtained to be 0.57 μ_B, the g value is calculated to be 0.66 assuming the relation $\mu_{eff}=g\sqrt{S(S+1)}$. This g value is reasonable for an f^1 electron perturbed by the octahedral crystal field [15–18] and comparable g values are found in many $5f^1$ compounds [16,17,19–22]. It is worth noting that the sign of the g value is expected to be negative for this $5f^1$ electronic configuration, which has been investigated using polarized microwave radiation for NpF_6 by Hutchison and Weinstock [16]. As will be shown later, the calculation result using Eq. (8) gives a negative g value for this $Ba_3ZnU_2O_9$.

Now we can determine the crystal field parameters and orbital reduction factors by fitting the calculated transition energies (Eq. (9)) to those determined experimentally [14] (Table 1) and by fitting the calculated g value (Eq. (8)) to that obtained from the magnetic susceptibility measurements ($|g|=0.66$). Table 1 lists the experimental and calculated electronic transition energies for $Ba_3ZnU_2O_9$. However, not all the calculated transition energies can be fitted to the experimental results. We have considered that the transition $\Gamma_7\rightarrow\Gamma'_8$ is the least reliable one because it is known to be broad and sometimes split. The crystal field parameters and orbital reduction factors determined from Eqs. (8) and (9) are also listed in Table 1. The spin–orbit coupling constant is 1939 cm^{-1}, which is a reasonable value for U^{5+} in solids [23–27], and is close to the value obtained from linear interpolation of the ζ values between Pa^{4+} and Np^{6+} compounds, 1950 cm^{-1} [28]. The orbital reduction factor for an electron in a Γ_4 orbital, $k'=0.80$, is in good agreement with those obtained for the $Ba_3CaU_2O_9$ and $Ba_3SrU_2O_9$ [8].

Fig. 4 shows the variation of g value for the ground Γ_7 doublet calculated from Eq. (8) (in the case of $k=1$) as a function of the relative strength of the crystal field and spin–orbit interaction, $\Delta/(7/2\zeta)$. This figure indicates

Table 1
Crystal field parameters and orbital reduction factors

	Experiment	Calculation
$\Gamma_7\rightarrow\Gamma_8$ (cm^{-1})	5605 [a]	5493
$\Gamma_7\rightarrow\Gamma'_7$ (cm^{-1})	7435	7435
$\Gamma_7\rightarrow\Gamma'_8$ (cm^{-1})	12990	13412
$\Gamma_7\rightarrow\Gamma_6$ (cm^{-1})	15630	15630
g value	$\lvert g\rvert=0.66$ [b]	$g=-0.66$
ζ (cm^{-1})		1939
Δ (cm^{-1})		4157
Θ (cm^{-1})		7022
k		1.0
k'		0.8

[a] According to Ref. [14], this transition is split into two transitions. This transition energy is the average value of individual energies.

[b] This g value was determined from the temperature-dependent part of the magnetic susceptibility (see text).

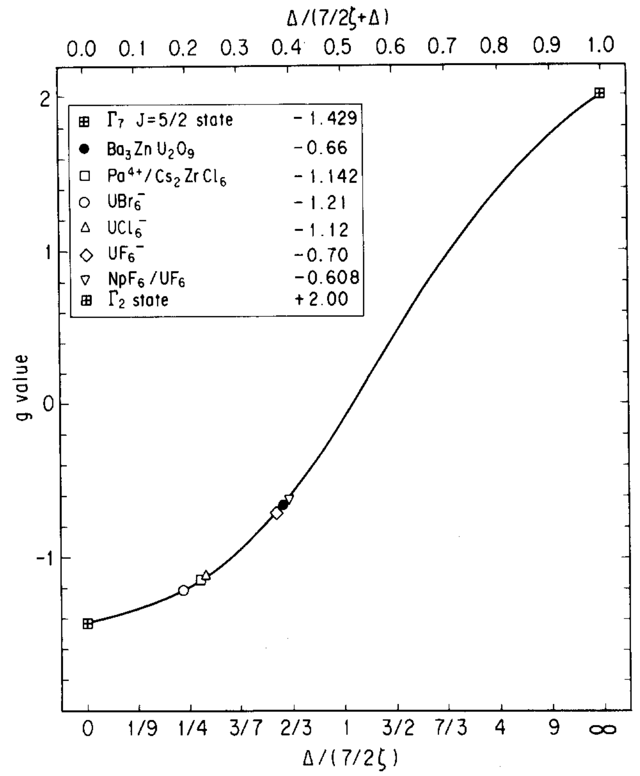

Fig. 4. Plot of g value vs. relative strength of crystal field and spin–orbit interaction, $\Delta/(7/2\zeta)$.

that the g value for an f electron perturbed by the octahedral crystal field should be between -1.43 and 2.00. In the figure, the g value determined for $Ba_3ZnU_2O_9$ is plotted along with the other compounds [16,19–21,28,29]. This g value is between the values for Pa^{4+} in Cs_2ZrCl_6 (weak crystal field) [29] and for Np^{6+} in UF_6 (strong crystal field) [16].

Since we have obtained the wavefunctions and energies for the ground and excited states, the magnetic susceptibility of $Ba_3ZnU_2O_9$ is easily calculated. The magnetic susceptibility of the molecule is given by the equation,

$$\chi = \frac{N\sum_{n,m}\{(E^{(1)}_{n,m})^2/kT - 2E^{(2)}_{n,m}\}\exp(-E^0_{n,m}/kT)}{\sum_{n,m}\exp(-E^0_{n,m}/kT)} \tag{10}$$

where N is the Avogadro's number, $E^0_{n,m}$ is the zero-field energy, $E^{(1)}_{n,m}$ and $E^{(2)}_{n,m}$ are the first- and second-order Zeeman terms, n and m are quantum numbers, and k is the Boltzmann's factor. If the separation of levels within the ground state is much smaller than, and the energy of the next excited state is much larger than kT, the susceptibility is expressed by the following form [30]:

$$\chi = \frac{Ng^2\beta^2}{4kT} + \chi_{\mathrm{TIP}} \tag{11}$$

where

$$\chi_{\mathrm{TIP}} = 2N\beta^2\sum_i \frac{|\langle\Gamma_i|L+2S|\Gamma_7\rangle|^2}{E(\Gamma_i)-E(\Gamma_7)} \tag{12}$$

The g value in Eq. (11) is the same as that for the ground crystal field state Γ_7 (Eq. (8)), i.e. the g value for the ground state can be determined from the temperature-dependent part of the susceptibility, as described already.

Next we will consider the temperature-independent susceptibility. From Eq. (12), it is calculated to be 208×10^{-6} emu/mol, which is near the experimentally estimated value, 290×10^{-6} emu/mol. The excess temperature-independent susceptibility found in this $Ba_3ZnU_2O_9$ is, we consider, ascribable to the magnetic property of U^{4+} ions formed owing to the oxygen nonstoichiometry. The U^{4+} ion ([Rn]$5f^2$ electronic configuration) in a crystal field with octahedral symmetry is known to show temperature-independent paramagnetism (TIP) over a wide temperature range, e.g. as found in $BaUO_3$ [7].

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