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Magnetic Properties of Ordered Perovskites $Ba_3CaU_2O_9$ and $Ba_3SrU_2O_9$

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Uranium complex oxides with the ordered perovskite structure, $Ba_3CaU_2O_9$, and $Ba_3SrU_2O_9$, were prepared, and their magnetic susceptibilities were measured in the temperature range between 4.2 K and room temperature. No magnetic cooperative phenomenon was found down to 4.2 K. The effective magnetic moments of $Ba_3CaU_2O_9$ and $Ba_3SrU_2O_9$ were 1.24 μ_B and 0.56 μ_B, respectively. Electron paramagnetic resonance (EPR) measurements were carried out for these compounds, but no EPR spectra which are ascribable to the U^{5+} ion in an octahedral crystal field were observed. The crystal field parameters of these compounds were determined from the analysis of the optical absorption spectra published previously. The effective moments and temperature-independent paramagnetic susceptibilities were calculated and compared with the experimental results.

INTRODUCTION

Actinide complex oxides with one or more metal ions in addition to an actinide are important because they may be found as fission products in nuclear fuels and because they are models for possible matrixes in which nuclear wastes are stored. Of many oxides, the mixed metal oxides ABO_3 (A = Ba, Sr) with perovskite structure are known to incorporate various kinds of tetravalent actinide ions at the B sites of the crystal (1). One interesting feature in these oxides is that "ordered" perovskites $A_2M^{3+}M^{5+}O_6$ ($A_2M^{2+}M^{6+}O_6$) are obtained by replacing the +4 cations in the $A^{2+}M^{4+}O_3$ perovskite compounds with +3 and +5 cations (or with +2 and +6 cations) (2).

The ordered perovskites based on the $BaUO_3$ attract our attention, because replacing half of the uranium ions with trivalent rare earth ions forms the ordered perovskites $Ba_2M^{3+}U^{5+}O_6$, oxidizing the rest of the uranium ions to the pentavalent state (3, 4). In a preceding paper (5), we reported the formation of such ordered perovskites and examined their magnetic properties through magnetic susceptibility and electron paramagnetic resonance (EPR) measurements.

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 metal), i.e., replacing one-third of the uranium ions with divalent alkaline earth ions also forms ordered perovskites. Since the oxygen stoichiometric $BaUO_3$ shows temperature-independent paramagnetism over a wide temperature range (6) and since hexavalent uranium ion is diamagnetic, the magnetic properties of U^{5+} in the Ba_2MUO_6 should be quite different from those of U^{4+} and U^{6+}, and therefore their magnetic study is very useful in elucidating the electronic state of uranium ions in these compounds. In this study, we prepared $Ba_3CaU_2O_9$ and $Ba_3SrU_2O_9$, and measured their magnetic susceptibilities in the temperature range between 4.2 K and room temperature, and their electron paramagnetic resonance spectra both at room temperature and at 4.2 K. Because the optical absorption spectra are available for these compounds (7), we determine the energy state of the U^{5+} ion in the compounds and evaluate the magnetic susceptibilities measured here.

EXPERIMENTAL

1. Preparation

As the starting materials, $BaCO_3$, CaO (SrO), and U_3O_8 were used. Before use, $BaCO_3$ and CaO (SrO) were heated in air at 800°C to remove any moisture, and U_3O_8 was oxidized in air at 850°C to form a stoichiometric compound. The $BaCO_3$, CaO (SrO), and U_3O_8 were weighed in the stoichiometric metal ratio, Ba : Ca(Sr) : U = 3 : 1 : 2. After being finely ground in an agate mortar, the mixtures were pressed into pellets and heated in a hydrogen gas flowing atmosphere at 1200°C for 10 hr. Then, the samples were cooled to room temperature, crushed into powder, re-pressed into pellets, and heated in an argon gas flowing atmosphere at 1300°C for 10 hr. After cooling to room temperature, the samples were re-crushed, re-pressed into pellets, and heated again in an argon gas atmosphere at 1300°C to make the reaction complete.

2. Analysis

2.1. X-ray diffraction analysis. An X-ray diffraction analysis was performed with CuKα radiation on a Philips

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TABLE 1
Lattice Parameter and Effective Magnetic Moment of $Ba_3MU_2O_9$

Compound	a(Å)	$\mu_{eff}(\mu_B)$
$Ba_3CaU_2O_{8.910}$	8.695	1.24
$Ba_3SrU_2O_{8.946}$	8.816	0.56

PW 1390 diffractometer equipped with a curved graphite monochromator. The lattice parameters of the samples were determined by a least-squares method.

2.2 Determination of oxygen amount. The volatilization of alkaline earth elements and uranium in the compounds during heating is negligible under these preparation conditions. The oxygen nonstoichiometry in the sample was checked by the back-titration method (8, 9). A weighed amount of sample was dissolved in an excess cerium(IV) sulfate solution, which was standardized in advance with stoichiometric UO_2. The remaining cerium(IV) was titrated against a standard iron(II) ammonium sulfate solution with the ferroin indicator. The oxygen amount was evaluated for each predetermined Ba : M : U ratio.

3. Magnetic Susceptibility Measurement

The magnetic susceptibility was measured by a Faraday-type torsion balance in the temperature range between 4.2 K and room temperature. The apparatus was calibrated with a Manganese Tutton's salt ($\chi_g = 10.98 \times 10^{-3}/(T + 0.7)$). The temperature of the sample was measured by a "normal" Ag vs Au–0.07 at. % Fe thermocouple (4.2 ~ 40 K) (10) and an Au–Co vs Cu thermocouple (10 K ~ room temperature). Details of the experimental procedure have been described elsewhere (11).

4. Electron Paramagnetic Resonance Measurement. The EPR measurements were carried out both at room temperature and at 4.2 K using a JEOL RE-2X spectrometer operating at X-band frequency (9.1 GHz) with 100 kHz field modulation. The magnetic field was swept from 100 to 13,000 G. Before the specimen was measured, a blank was recorded to eliminate the possibility of interference by the background resonance of the cavity and/or the sample tube. The magnetic field was monitored with a proton NMR gaussmeter, and the microwave frequency was measured with a frequency counter.

RESULTS AND DISCUSSION

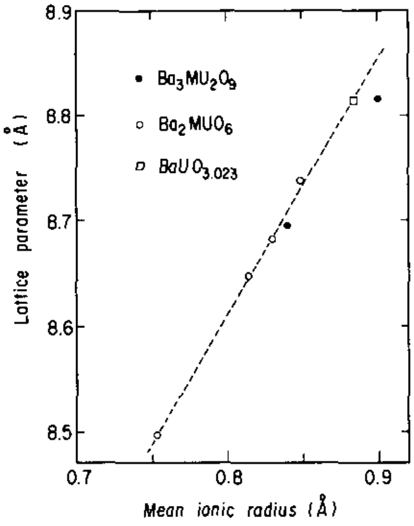

FIG. 1. Lattice parameters of Ba_2MUO_6 and $Ba_3MU_2O_9$ vs mean ionic radius of the ions at the B sites of the perovskite crystal. The lattice parameter shown for $BaUO_{3.023}$ is twice the actual lattice parameter (4.4075 Å).

Two complex oxides prepared in this study, $Ba_3CaU_2O_9$ and $Ba_3SrU_2O_9$, are listed in Table 1. They are cubic with the ordered perovskite structure. From the results of oxygen analysis, we can say that they are nearly oxygen stoichiometric, although some oxygen deficiency is found. In these oxides, both Ca^{2+} (Sr^{2+}) and U^{5+} ions occupy the B sites of the perovskite ABO_3. Figure 1 shows the lattice parameters of $Ba_3MU_2O_9$ compounds against a mean ionic radius r of the ions at the B sites in the crystal (i.e., $r = (r(M^{2+}) + 2r(U^{5+}))/3$). In this figure, the lattice parameters of $Ba_2M^{3+}U^{5+}O_6$ compounds (5) are also plotted. The lattice parameters of the latter compounds are linear against the mean radius of B-site ions, indicating that the lattice parameter change among Ba_2MUO_6 compounds depends only on the ionic radius of the ions at the B sites of the crystals. Twice the lattice parameter of the basic lattice $BaUO_3$ (6) also follows this linear relation (see Fig. 1; actually, a = 4.4075 Å for $BaUO_{3.023}$ (6)). Roughly speaking, the lattice parameters for the compounds prepared in this study may follow the same relation (the broken line in Fig. 1), but actually the lattice parameter of $Ba_3SrU_2O_9$ is below this line, which means that the effect of Sr^{2+} substitution for U^{4+} on the size of the ordered perovskite is not so simple as the case of M^{3+} substitution because of the large difference in ionic radius between Sr^{2+} and U^{5+} ions.

The oxidation state of uranium ions in these nearly oxygen-stoichiometric compounds is considered to be pentavalent from the charge neutrality conditions, which is strongly supported by the magnetic susceptibility measurements. Figure 2 shows the variation of reciprocal magnetic susceptibility with temperature for $Ba_3CaU_2O_9$ and $Ba_3SrU_2O_9$. No magnetic cooperative phenomenon was found down to 4.2 K. The susceptibilities of these compounds are both temperature dependent, in contrast to the temperature-independent paramagnetism (TIP) of oxygen-stoichiometric $BaUO_3$ (6). This result indicates that the possibility of oxidation species $Ba_3M^{2+}U^{4+}U^{6+}O_9$ should be excluded, because in that case their magnetic properties are expected to be similar to that of $BaUO_3$ (U^{6+} is diamagnetic). Their susceptibilities do not follow the Curie–Weiss law. By extrapolating the reciprocal temperature $1/T$ to zero for the susceptibility vs reciprocal temperature curves, we obtain the temperature-independent paramagnetic susceptibilities 430×10^{-6} and 310×10^{-6} emu/mole for $Ba_3CaU_2O_9$ and $Ba_3SrU_2O_9$, respectively. These TIP values are, of course, much smaller than that for $BaUO_3$ ($1{,}110 \times 10^{-6}$ emu/mole) (6). From the temperature-dependent part of the susceptibility, the effective magnetic moments for $Ba_3CaU_2O_9$ and $Ba_3SrU_2O_9$ are calculated to be 1.24 μ_B (70–300 K) and 0.56 μ_B (50–300 K), respectively. These values are much smaller than that for the moment for a free f^1 ion, U^{5+} (2.54 μ_B), which indicates that the crystal field effect on the magnetic properties of an f electron is large. Similar small magnetic moments have been reported for U^{5+} and other ternary oxides with the same $5f^1$ electronic configuration (12).

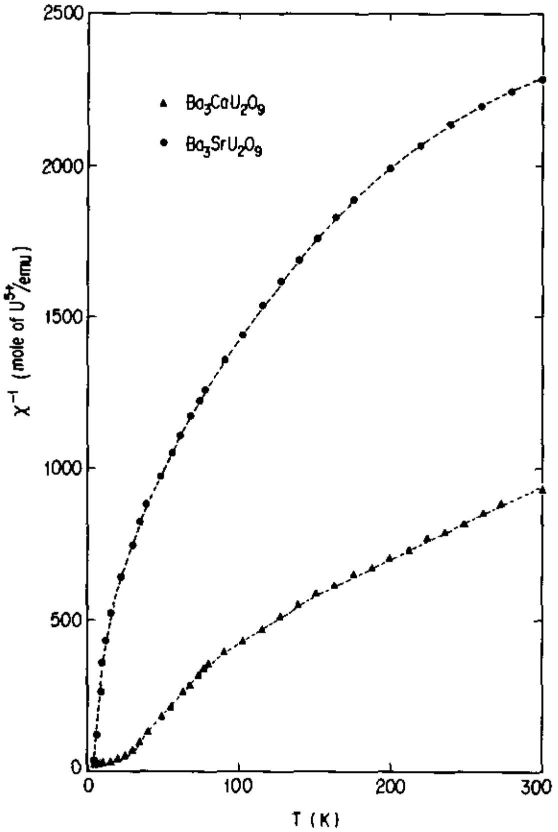

FIG. 2. Temperature dependence of reciprocal magnetic susceptibilities of $Ba_3CaU_2O_9$ and $Ba_3SrU_2O_9$.

Since the absorption spectra are available for these compounds (7), we can determine the crystal field energy levels and then calculate the magnetic susceptibility. In these compounds, the U^{5+} ions are in the octahedral crystal field by six oxygen ions.

Figure 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 sevenfold 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 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

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

$$\Gamma_8: \begin{vmatrix} \Delta + \frac{1}{4}k\zeta & \frac{3}{4}\sqrt{5kk'}\zeta \\ \frac{3}{4}\sqrt{5kk'}\zeta & \Delta + \Theta - \frac{3}{4}k'\zeta \end{vmatrix} \tag{1}$$

$$\Gamma_6: \begin{vmatrix} \Delta + \Theta + \frac{3}{2}k'\zeta \end{vmatrix}.$$

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 (13). Diagonalization of the energy matrix produces the ground state Γ_7 and the excited state Γ_7', and the corresponding wavefunctions are written as

$$\begin{aligned} |\Gamma_7\rangle &= \cos\theta|^2F_{5/2}, \Gamma_7\rangle - \sin\theta|^2F_{7/2}, \Gamma_7^*\rangle, \\ |\Gamma_7'\rangle &= \sin\theta|^2F_{5/2}, \Gamma_7\rangle + \cos\theta|^2F_{7/2}, \Gamma_7^*\rangle, \end{aligned} \tag{2}$$

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

$$\tan 2\theta = \frac{2\sqrt{3}k\zeta}{\Delta - \frac{1}{2}k\zeta}. \tag{3}$$

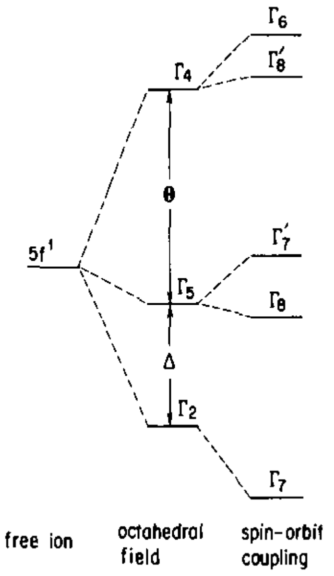

FIG. 3. f^1 orbital splitting perturbed by octahedral crystal field and spin-orbit coupling.

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

$$\begin{aligned} g &= 2\langle\Gamma_7|\mathbf{L} + 2\mathbf{S}|\Gamma_7\rangle \\ &= 2\cos^2\theta - 4\sqrt{\frac{k}{3}}\sin 2\theta - \frac{2}{3}(1-k)\sin^2\theta. \end{aligned} \tag{4}$$

The energies for the Γ_7, Γ_8, Γ_7', Γ_8', and Γ_6 (in the order of ascending energies) are

$$\begin{aligned} E(\Gamma_7) &= \Delta - \frac{1}{2}\{k + 2\sqrt{3k}\cot\theta\}\zeta \\ E(\Gamma_8) &= \Delta + \Theta - \frac{3}{4}\{k' + \sqrt{5kk'}\cot\varphi\}\zeta \\ E(\Gamma_7') &= \sqrt{3k}\,\zeta\cot\theta \\ E(\Gamma_8') &= \Delta + \frac{1}{4}\{k + 3\sqrt{5kk'}\cot\varphi\}\zeta \\ E(\Gamma_6) &= \Delta + \Theta + \frac{3}{2}k'\zeta, \end{aligned} \tag{5}$$

where φ is the parameter describing the admixture of the Γ_8 levels in the excited state. We apply the above-mentioned treatments to the energy level analysis for $Ba_3CaU_2O_9$ and $Ba_3SrU_2O_9$.

First, we consider the case of the $Ba_3SrU_2O_9$ compound. Since the effective magnetic moment of the U^{5+} ion is found to be 0.56 μ_B from the temperature-dependent part of the susceptibility, the g value is calculated to be 0.65 assuming the relation $\mu_{eff} = g\sqrt{S(S+1)}$. This g value is reasonable for an f^1 electron in an octahedral crystal field (13–15) and is often found for U^{5+} compounds (16–20). 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 (14). As is described later, the calculation result using Eq. (4) gives a negative g value for this $Ba_3SrU_2O_9$. Now, we can use both the optical absorption spectrum and EPR spectrum data to analyze the crystal field energy levels. The crystal field parameters and orbital reduction factors obtained are listed in Table 2. The spin-orbit coupling constant is 1909 cm^{-1}, which is a reasonable value for U^{5+} in solids (21–23), and is close to the value obtained from linear interpolation of the ζ values between Pa^{4+} and Np^{6+} compounds, 1950 cm^{-1} (24). The obtained orbital reduction factor, $k' = 0.80$, for an electron in a Γ_4 orbital has also been calculated for the same Γ_4 orbital in a Li_7UO_6 compound (25). As shown in Table 3, the transition energies calculated from these crystal field parameters and the g value of EPR are fitted to the experimental data except the $\Gamma_7 \rightarrow \Gamma_8'$ transition. Since the transition $\Gamma_7 \rightarrow \Gamma_8'$ for octahedral symmetry is known to be broad and since this transition is furthermore broadened even due

TABLE 2
Crystal Field Parameters and Orbital Reduction Factors

Compound	$\zeta(cm^{-1})$	$\Delta(cm^{-1})$	$\Theta(cm^{-1})$	k	k'
$Ba_3CaU_2O_9$	1950	3949	7000	1	0.8
$Ba_3SrU_2O_9$	1909	4089	7000	1	0.8

TABLE 3
Electronic Transition Energies

Compound	Assignment	Transition energies (cm^{-1}) Experimental[a]	Transition energies (cm^{-1}) Calculation
$Ba_3CaU_2O_9$	$\Gamma_7 \rightarrow \Gamma_6$	15152	15492
	$\Gamma_7 \rightarrow \Gamma_8'$	10935	13271
	$\Gamma_7 \rightarrow \Gamma_7'$	7380	7368
	$\Gamma_7 \rightarrow \Gamma_8$	5538	5350
$Ba_3SrU_2O_9$	$\Gamma_7 \rightarrow \Gamma_6$	15385	15476
	$\Gamma_7 \rightarrow \Gamma_8'$	10760	13279
	$\Gamma_7 \rightarrow \Gamma_7'$	7326	7326
	$\Gamma_7 \rightarrow \Gamma_8$	5367	5422

[a] These values are obtained from Fig. 2 of Ref. (7). Actually, some of the transitions are split into two or three transitions. In this case, the transition energy is the average value of individual transition energies.

to small crystal field distortion, we have considered the $\Gamma_7 \rightarrow \Gamma_8'$ transition energy to be the least reliable.

Next we consider the temperature-independent susceptibility. Since this value is given by the equation (26)

$$\chi_{\mathrm{TIP}} = 2N\beta^2 \sum_i \frac{|\langle \Gamma_i | \mathbf{L} + 2\,\mathbf{S} | \Gamma_7 \rangle|^2}{E(\Gamma_i) - E(\Gamma_7)}, \tag{6}$$

it is calculated to be 241 × 10^{-6} emu/mole, which is near the value from experiment, 310 × 10^{-6} emu/mole. The excess temperature-independent susceptibility obtained from experiment is 69 × 10^{-6} emu/mole. We consider that this excess temperature independent paramagnetism is ascribable to the magnetic property of U^{4+} ions formed due to the oxygen nonstoichiometry in $Ba_3SrU_2O_9$. The U^{4+} ion ($5f^2$ electronic configuration) in a crystal field with octahedral symmetry shows temperature-independent paramagnetism (TIP) over a wide temperature range (27), and the temperature-independent susceptibility of oxygen-stoichiometric $BaUO_3$ is $\chi_{\mathrm{TIP}} = 1.11 \times 10^{-3}$ emu/mole (6). From the ratio of the excess temperature-independent susceptibility to the susceptibility of $BaUO_3$, the ratio of the uranium ions at the tetravalent state is 6.1%. This value is comparable to the ratio of U^{4+} ion (5.4%) calculated from the oxygen nonstoichiometry of $Ba_3SrU_2O_9$.

To obtain the information on the ground Γ_7 state, EPR measurements were carried out for $Ba_3SrU_2O_9$. No EPR spectrum was observed at room temperature. At 4.2 K, one weak broad spectrum was observed around ca. 3150 G, the g value of which was ca. 2.1. From Eq. (4), the g value for an f^1 electron in an octahedral crystal field should be less than two (15), and most of the experimental results for the $5f^1$ compounds have given g values between 0.6 and 1.2 (as the absolute value) (14, 16–20, 23, 24, 28–30). Therefore, we have considered that the EPR spectrum measured is not ascribable to the magnetic property of the U^{5+} ion in an octahedral crystal field. Several researchers reported that some pure uranium compounds have given broad EPR spectra, the g values of which are larger than two (31–35). In these compounds, the U^{5+} ion is in an octahedral crystal field. We have considered that similar experimental conditions to measure the EPR spectrum ($g > 2$) might be valid for our case.

Next, we discuss the case of the $Ba_3CaU_2O_9$ compound. The same calculation was performed for the optical absorption spectrum of $Ba_3CaU_2O_9$ (7). Since the optical absorption spectrum of $Ba_3CaU_2O_9$ is quite similar to that of $Ba_3SrU_2O_9$, i.e., the transition energies from the ground state to the excited states are comparable between these two compounds, it is predicted that there are not many differences in the crystal field parameters between $Ba_3CaU_2O_9$ and $Ba_3SrU_2O_9$ (Table 2). The energy fitting to the $\Gamma_7 \rightarrow \Gamma_8'$ transition is still bad (Table 3). The crystal field at the U^{5+} site in $Ba_3CaU_2O_9$ is expected to be stronger than that in $Ba_3SrU_2O_9$ because of the smaller lattice parameter (see Table 1). If we accept the g value of U^{5+} in $Ba_3SrU_2O_9$ to be −0.65, which is derived from the calculation, then, with a stronger crystal field, the g value of U^{5+} in the octahedral crystal field of $Ba_3CaU_2O_9$ should be less negative than −0.65. We have previously shown that the g value for an f electron in an octahedral crystal field should be between −1.43 and 2.00 (15). Thus the g value of U^{5+} in $Ba_3CaU_2O_9$ should be between −0.65 and 2.00. However, the g value calculated from the crystal field parameters using Eq. (4) is −0.711, which deviates from the above expectation. We consider that this is due to the inappropriate crystal field parameters because they are only calculated from the optical absorption spectrum. In spite of a large difference in the temperature-dependent magnetic susceptibility between $Ba_3CaU_2O_9$ and $Ba_3SrU_2O_9$, the transition energies observed (therefore the crystal field parameters) for $Ba_3CaU_2O_9$ are similar to those for $Ba_3SrU_2O_9$. We have considered that the optical absorption spectrum measured by Kemmler-Sack and Wall (7) needs verifying. The absolute g value is also calculated from the effective magnetic moment and it is 1.43. However, it is not likely that the g value could be as large as +1.43, which implies a very much stronger crystal field than that found in $Ba_3SrU_2O_9$. If the crystal field is zero, then the g value of the Γ_7 state is −1.43; again this is not possible for the U^{5+} ion in $Ba_3CaU_2O_9$. Based on the above argument, it appears that this simple crystal field model for a U^{5+} ion in octahedral symmetry is not adequate for the $Ba_3CaU_2O_9$ compound. Something more complex is occurring and contributes to the magnetic susceptibility of $Ba_3CaU_2O_9$. No EPR spectrum was observed even at 4.2 K.

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