

Magnetic Susceptibility of $\text{Ba}_2\text{YbTaO}_6$ with the Ordered Perovskite Structure and Electron Paramagnetic Resonance of Yb^{3+} Doped in $\text{Ba}_2\text{LuTaO}_6$

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A quaternary oxide, $\text{Ba}_2\text{YbTaO}_6$, was prepared, and its powder X-ray diffraction measurements and the Rietveld analysis show that it is cubic with the space group $Fm\bar{3}m$ and that Yb^{3+} and Ta^{5+} ions are structurally ordered. Magnetic susceptibilities of $\text{Ba}_2\text{YbTaO}_6$ were measured in the temperature range between 5 K and room temperature, and the electron paramagnetic resonance (EPR) spectrum of Yb^{3+} ion doped in $\text{Ba}_2\text{LuTaO}_6$ was measured at 8 K. This compound is paramagnetic down to 5 K, and the temperature dependence of its susceptibility was analyzed with the crystal field model. Hyperfine interaction was observed for the EPR spectrum of $\text{Yb}^{3+}/\text{Ba}_2\text{LuTaO}_6$. Analysis of the EPR data indicates the existence of the covalency in the Yb^{3+} ion in an octahedral symmetry. © 2000 Academic Press

INTRODUCTION

The electronic configuration of an Yb^{3+} ion is $[\text{Xe}]4f^{13}$ ($[\text{Xe}]$: Xenon electronic core). This f^{13} configuration is simple; i.e., this is equivalent to the case that there is one hole in the closed $4f$ electron shell (f^{14} configuration). Therefore, we need not consider the effect of electron repulsion interaction in the analysis of the electronic state of the $4f$ electron in solids. In particular, when this ion is located in an octahedral crystal field environment, such a compound is suitable for studying the behavior of $4f$ electrons in solids because it is easy to compare the experimental results with theoretical calculations.

However, trivalent rare earth ions are not usually found in sites of octahedral symmetry because their ionic radii are so large that more than six anions are easily coordinated to the rare earth ions. They may be forced to occupy such high symmetry sites (octahedral or cubic) by doping them into various cubic crystals such as alkaline earth oxides and halides. In these cases, however, there is always the problem of charge compensation, and there is more than one type of site present and this leads to more complications.

We have been interested in the “double perovskites” (1) as one of the candidate host materials in which “trivalent” rare earth ions are incorporated at the sites of octahedral symmetry. The simple perovskite oxides have the general formula ABO_3 , in which A represents a large electropositive cation and B represents a small cation such as a transition metal ion. The perovskite structure can be described as a framework of corner-shared BO_6 octahedra which contain A cations at 12-coordinate sites. Large cations such as rare earth ions usually occupy the A sites of the perovskite. When larger alkaline earth elements (e.g., Sr, Ba) occupy the A sites, “tetravalent” rare earth ions are incorporated into the B sites of the perovskite. Double perovskite-type oxides have the formula $\text{A}_2\text{B}'\text{B}''\text{O}_6$, in which the primes indicate the different ions in different oxidation states, and in some cases, the cations at the B sites, B' and B'' , regularly order. When alkaline earth elements occupy the A sites and when transition metal ions in the pentavalent state have been selected at the B'' cation of the $\text{A}_2\text{B}'\text{B}''\text{O}_6$ compounds, trivalent rare earth ions may be incorporated at the B' sites and the B' and B'' ions regularly order in the NaCl type, over the six-coordinate B sites. In addition, if the diamagnetic transition metal ions such as Nb^{5+} and Ta^{5+} have been selected at the B'' site ions, only the B' ions are responsible for the magnetic properties of double perovskites.

In this study, we prepared a quaternary oxide, $\text{Ba}_2\text{YbTaO}_6$, and determined its crystal structure by X-ray diffraction measurements. The magnetic susceptibility has been measured in the temperature range between 5 K and room temperature. To elucidate the electronic state of the Yb^{3+} ion in solids, we prepared a sample in which an Yb^{3+} ion is doped in a diamagnetic $\text{Ba}_2\text{LuTaO}_6$ (where the Yb^{3+} ion is substituted for the Lu^{3+} ion) and measured its electron paramagnetic resonance (EPR) spectrum at 8 K. The temperature dependence of the susceptibility for $\text{Ba}_2\text{YbTaO}_6$ has been analyzed by using the data obtained from the EPR measurements on $\text{Yb}^{3+}/\text{Ba}_2\text{LuTaO}_6$.

EXPERIMENTAL

1. Sample Preparation

Two samples, $\text{Ba}_2\text{YbTaO}_6$ and $\text{Ba}_2\text{Yb}_{0.02}\text{Lu}_{0.98}\text{TaO}_6$ (for EPR measurements), were prepared in this study. As starting materials, BaCO_3 , Yb_2O_3 , Lu_2O_3 , and Ta_2O_5 were used. Before use, the Yb_2O_3 , Lu_2O_3 , and Ta_2O_5 were heated in air at 850°C to remove any moisture and oxidized to the stoichiometric compositions. BaCO_3 was also heated in air at 300°C to remove any moisture. They were weighed in the appropriate metal ratios and intimately mixed in an agate mortar. The mixtures were pressed into pellets and then heated in air at 1300°C for 72 h. After being cooled to room temperature, the pellets were crushed into powder, reground, repressed into pellets, and heated again at 1500°C for 24 h to make the reaction complete.

2. X-ray Diffraction Measurements

An X-ray diffraction analysis was performed with $\text{CuK}\alpha$ radiation on a RINT 2000 diffractometer equipped with a curved graphite monochromator. The data were collected by step scanning over a range $10^\circ \leq 2\theta \leq 120^\circ$ in increments of 0.02° (2θ). The structure and lattice parameters were refined with a Rietveld program RIETAN (2).

3. Magnetic Susceptibility Measurements

Magnetic susceptibility measurements were made using a SQUID magnetometer (Quantum Design MPMS). A susceptibility–temperature curve was measured under both the ZFC (zero-field-cooled) and the FC (field-cooled) conditions. The former was measured upon heating the sample to 300 K after zero-field-cooling to 5 K, applying a field of 1000 G. The latter was measured upon cooling from 300 to 5 K at 1000 G.

4. Electron Paramagnetic Resonance Measurement

The EPR spectra at the X band (9.096 GHz) were measured using a JEOL RE-2X spectrometer operating with an Air Products Helitran cooling system. The magnetic field was swept from 100 to 13,500 G, which was monitored with a proton NMR gaussmeter, and the microwave frequency was measured with a frequency counter. Before the samples were measured, a blank was recorded to eliminate the possibility of interference by the background resonance of the cavity and/or the sample tube.

RESULTS AND DISCUSSION

X-ray diffraction measurements show that $\text{Ba}_2\text{YbTaO}_6$ prepared in this study was formed in a single phase with a cubic unit cell. Figure 1 shows its X-ray diffraction profile.

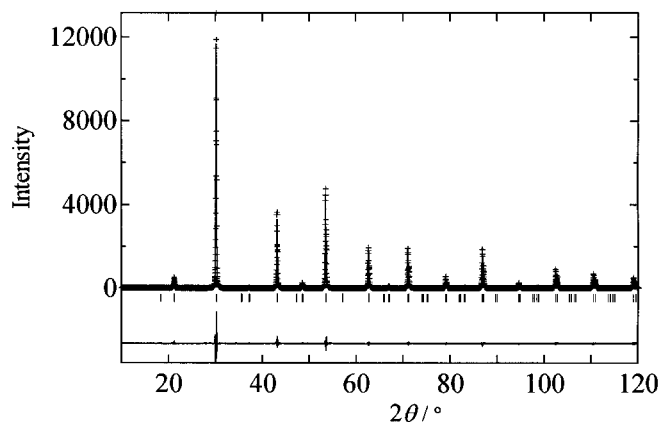


FIG. 1. Observed and calculated X-ray diffraction profiles for $\text{Ba}_2\text{YbTaO}_6$. The observed data are indicated by crosses, and the calculated profile is the solid line. The short vertical lines below the profiles mark the positions of all possible Bragg reflections. The bottom continuous line is the difference between the observed and calculated intensities.

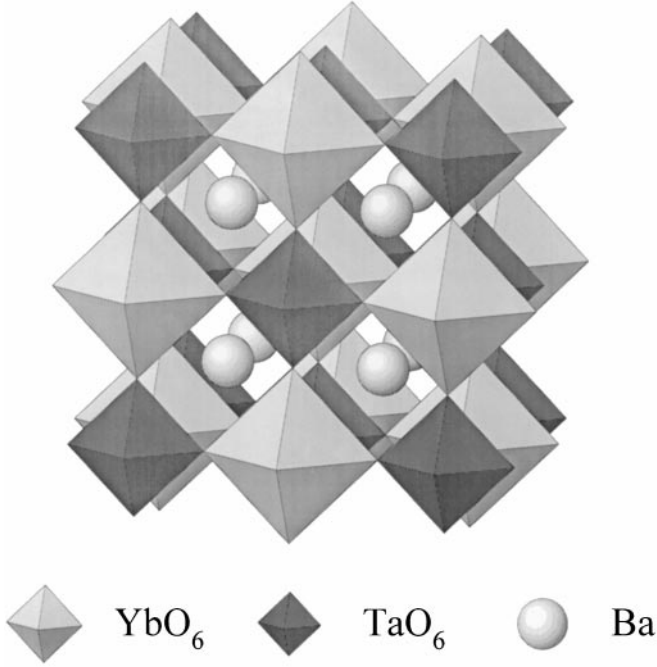
The diffraction profile shows the existence of a superlattice reflection at $2\theta = 18.28^\circ$, indicating that this compound is an ordered perovskite and its lattice parameter is double the lattice parameter of the primitive perovskite; $a = 2a_p$ (a_p is the lattice parameter of the cubic perovskite unit cell). We have performed the Rietveld analysis for the X-ray diffraction profile. The lattice parameter and atomic parameters after refinements are listed in Table 1. The lattice parameter for this $\text{Ba}_2\text{YbTaO}_6$ is determined to be $a = 8.3903 \text{ \AA}$, in excellent agreement with that reported by other workers (3). The structure was refined by applying the space group $Fm\bar{3}m$. This space group allows two crystallographically distinct octahedral sites in the perovskite structure, thus permitting 1:1 positional ordering between the B-site ions, Yb^{3+} and Ta^{5+} ions. Figure 2 depicts the crystal structure of $\text{Ba}_2\text{YbTaO}_6$.

Figure 3 shows the temperature dependence of the magnetic susceptibility measured for $\text{Ba}_2\text{YbTaO}_6$. This

TABLE 1
Lattice Parameters and Atomic Positions for $\text{Ba}_2\text{YbTaO}_6$

Atom	Site	x	y	z	B (\AA^2)
Atomic Parameters for $\text{Ba}_2\text{YbTaO}_6$ at Room Temperature space group $Fm\bar{3}m$ (No. 225) $a = 8.3903(1) \text{ \AA}$ $R_{\text{wp}} = 15.77$ $R_1 = 2.01$ $R_F = 4.06$					
Ba	8c	0.25	0.25	0.25	0.3
Yb	4b	0.5	0.5	0.5	0.3
Ta	4a	0	0	0	0.3
O	24e	0.237(7)	0	0	0.3

Note. Isotropic thermal parameters (B) are fixed to be 0.3 \AA^2 .


 FIG. 2. Crystal structure of the double perovskite Ba₂YbTaO₆.

compound is paramagnetic and shows no magnetic ordering in the temperature range studied.

A crystal field interaction of cubic symmetry is conveniently expressed in the equivalent operator form

$$H = B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4), \quad [1]$$

where the O_n^m operators describe the cubic symmetry of the crystal field and the factors B_4 and B_6 are parameters to be determined experimentally. Since we have only two parameters in Eq. [1], the energy levels and eigen functions can be computed numerically, on a reduced energy scale, for various values of the ratio of the two parameters. This has been carried out by Lea, Leask, and Wolf (4).

The free Yb³⁺ ion has the configuration $4f^{13}$, which gives rise to a $^2F_{7/2}$ ground multiplet and a $^2F_{5/2}$ excited multiplet at about 10,000 cm⁻¹. The $^2F_{5/2}$ has little effect on the magnetic properties.

In a cubic crystal field, the eight-fold ground-state degeneracy for the $^2F_{7/2}$ will be split into a pair of doublets, Γ_6 and Γ_7 , and a quartet Γ_8 . In a site for which the nearest-neighbor coordination is six-fold (i.e., in an octahedral symmetry), the ground state is most likely to be the Γ_6 . Figure 4 shows the energy level diagram for the configuration $4f^{13}$ in an octahedral crystal field. The wave functions for these states are

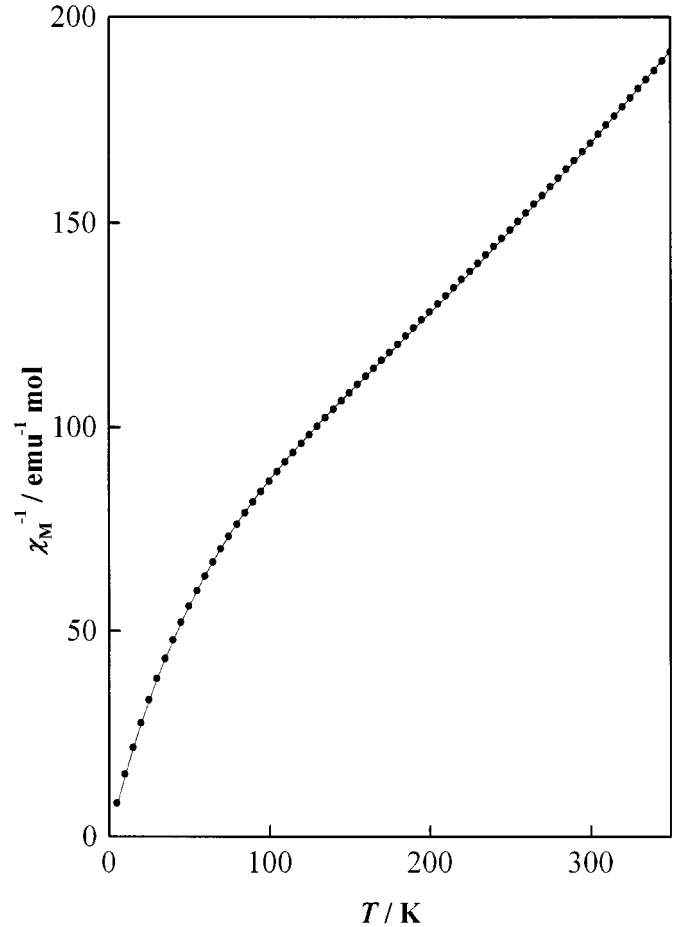
$$\text{ground state } \Gamma_6: \sqrt{5/12}|\pm 7/2\rangle + \sqrt{7/12}|\mp 1/2\rangle,$$

$$\begin{aligned} \text{1st excited state } \Gamma_8: & \sqrt{7/12}|\pm 7/2\rangle - \sqrt{5/12}|\mp 1/2\rangle \\ & 1/2|\pm 5/2\rangle + \sqrt{3/2}|\mp 3/2\rangle, \end{aligned}$$

$$\text{2nd excited state } \Gamma_7: \sqrt{3/2}|\pm 5/2\rangle - 1/2|\mp 3/2\rangle. \quad [2]$$

Since we have obtained the wave functions, the magnetic susceptibility is given by the following Van Vleck's equation (5),

$$\begin{aligned} \chi = & \frac{N\beta^2}{kT} [\sum |\langle \Gamma_6 | \mathbf{L} + 2\mathbf{S} | \Gamma_6 \rangle|^2 \\ & + \sum |\langle \Gamma_8 | \mathbf{L} + 2\mathbf{S} | \Gamma_8 \rangle|^2 \exp(-E_1/kT) \\ & + \sum |\langle \Gamma_7 | \mathbf{L} + 2\mathbf{S} | \Gamma_7 \rangle|^2 \exp(-E_2/kT)] / \\ & [n_0 + n_1 \exp(-E_1/kT) + n_2 \exp(-E_2/kT)] \\ & + 2N\beta^2 [\sum |\langle \Gamma_6 | \mathbf{L} + 2\mathbf{S} | \Gamma_8 \rangle|^2 (1 - \exp(E_1/kT))/E_1 \\ & + \sum |\langle \Gamma_8 | \mathbf{L} + 2\mathbf{S} | \Gamma_7 \rangle|^2 (\exp(-E_1/kT) \\ & - \exp(-E_2/kT)/(E_2 - E_1))] / \\ & [n_0 + n_1 \exp(-E_1/kT) + n_2 \exp(-E_2/kT)] \quad [3] \end{aligned}$$


 FIG. 3. Inverse susceptibility vs temperature for Ba₂YbTaO₆. A fit to Eq. [4] is shown with a solid line.

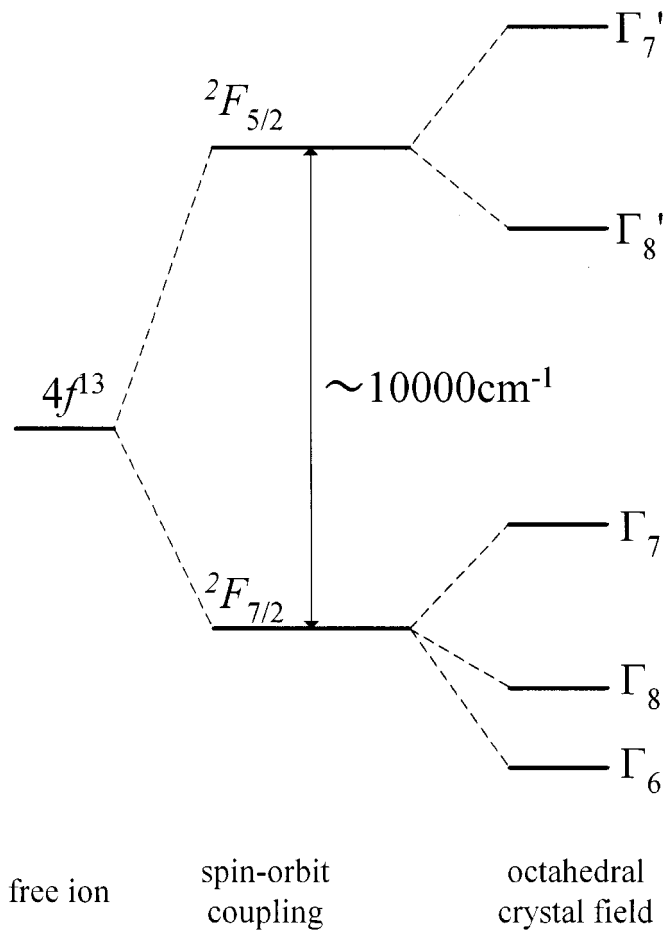


FIG. 4. The energy level diagram for the configuration $4f^{13}$ in an octahedral crystal field

where N is Avogadro's number, β is the Bohr magneton, E_1 is the energy difference between the Γ_6 ground state and the first excited Γ_8 , E_2 is the energy difference between the Γ_6 ground state and the second excited state Γ_7 , and n_0 , n_1 , and n_2 are the degeneracy of the ground state Γ_6 , the first excited state Γ_8 , and the second excited state Γ_7 , respectively. Evaluating the matrix elements and substituting numerical values into Eq. [2], we have the following equation as the magnetic susceptibility for $\text{Ba}_2\text{YbTaO}_6$,

$$\chi = \frac{g_J^2 \beta^2 J(J+1)}{3kT} F(T), \quad [4]$$

where

$$F(T) = [98 + 260 \exp(-E_1/kT) + 162 \exp(-E_2/kT) + \frac{432kT}{E_1 - E_2} (\exp(-E_2/kT) - \exp(-E_1/kT)) + \frac{560kT}{E_1} (1 - \exp(-E_1/kT))] / [378(1 + 2 \exp(-E_1/kT) + \exp(-E_2/kT))].$$

By fitting this Eq. [4] to the experimental susceptibility data, we have obtained $E_1 = 429.7 \text{ cm}^{-1}$, $E_2 = 1225.4 \text{ cm}^{-1}$, and $\mu_{\text{exp}} = 4.41 \mu_B$. The effective magnetic moment of Yb^{3+} determined from this susceptibility measurement is smaller than the calculated moment for the free ion ($4.54 \mu_B$), which means that the Yb^{3+} ion in $\text{Ba}_2\text{YbTaO}_6$ is affected by the crystal field to some extent. This result is consistent with the result by the EPR measurements of the $\text{Yb}^{3+}/\text{Ba}_2\text{LuTaO}_6$, as will be discussed later.

Figure 5 shows an EPR spectrum of a Yb^{3+} ion doped in $\text{Ba}_2\text{LuTaO}_6$ measured at 8 K. The spectrum is complicated and composed of many absorption lines. For ytterbium, there are seven isotopes. Among them, ^{171}Yb (natural abundance 14.3%) and ^{173}Yb (natural abundance 16.1%) have nuclear spins of $I = 1/2$ and $5/2$, respectively. The spin Hamiltonian for the EPR spectrum of $\text{Yb}^{3+}/\text{Ba}_2\text{LuTaO}_6$ is

$$H = g\beta\mathbf{H} \cdot \mathbf{S}' + A\mathbf{S}' \cdot \mathbf{I}, \quad [5]$$



FIG. 5. EPR spectrum of a Yb^{3+} ion doped in $\text{Ba}_2\text{LuTaO}_6$ measured at 8 K. Isotropic EPR absorption lines for $I = 1/2$ and $I = 5/2$ are depicted with the stick diagram below.

where g is the g value for Yb³⁺ with effective spin $S' = 1/2$ and nuclear spin $I = 0, 1/2, \text{ or } 5/2$, A is the hyperfine coupling constant, and H is the applied magnetic field. Usually, the assumption can be made that the electronic Zeeman term (the first term on the right-hand side of Eq. [5]) is much larger than the hyperfine term (the second term on the right-hand side), which would result in a six-line spectrum for an isotropic resonance with $I = 5/2$. The hyperfine spacings will be equal.

In the Yb³⁺/Ba₂LuTaO₆ crystal, the spacings between EPR absorption lines become wider with resonance magnetic field, which indicates that the electron spin quantum number (m_s) and the nuclear spin quantum number (m_I) are not good (pure) quantum numbers. We have to solve the Hamiltonian [5] exactly. The solution has been given by Ramsey (6) and others (7).

First, I and S are coupled together to form the resultant F , where $F = I + S$. For $S = 1/2$ and $I = 5/2$ in the absence of a magnetic field, there are two states, $F = 2$ and $F = 3$, which are separated by $3A$. When the magnetic field is included, each of these two states splits into $(2F + 1)|m_F\rangle$ Zeeman levels and six allowed transitions ($\Delta F = \pm 1$; $\Delta m_F = \pm 1$) are observable. For the case of ¹⁷¹Yb with $I = 1/2$, two transitions are observable.

The results of fitting the spin Hamiltonian (Eq. [5]) to the observed EPR spectra are shown in Table 2 and also in Fig. 5 by depicting the isotropic EPR absorption lines with the stick diagram. The g values and hyperfine coupling constants determined are $g = 2.536$ and $A = 0.0673$ for ¹⁷¹Yb; $g = 2.538$ and $A = 0.0185$ for ¹⁷³Yb; $g = 2.535$ for the Yb ion with even nuclear spins, respectively.

The ground state of Yb³⁺ in a pure octahedral crystal field is the Γ_6 state. In this case, the calculation of the g value is relatively simple; because the excited ²F_{5/2} state does not contain the Γ_6 representation, there is no admixture from this state. The Γ_6 state has an isotropic spectroscopic splitting factor in an applied magnetic field given by $g = 7/3 g_{\text{Lande}}$. Using $g_{\text{Lande}} = 8/7$, the predicted g value should be 2.667. When compared with this theoretical g value for the Γ_6 level, the experimental g value is smaller. This discrepancy provides evidence for the existence of the covalent bonding in the rare earth ions; i.e., the covalent contribution of the s and p orbitals from the O²⁻ ion to the empty $4f$ orbital of the Yb³⁺ ion causes a reduction of the

TABLE 2
Experimental and Calculated EPR Absorption Line Positions for Yb³⁺/Ba₂LuTaO₆ (All Values Are in Gauss)

Experimental	Calculated	Difference
¹⁷³ Yb ($I = 5/2$)		
$ g = 2.538, A = 0.0185 \text{ cm}^{-1}$		
2162	2157.74	4.26
2296	2294.80	1.20
2442	2441.53	0.47
2596	2597.98	1.88
2767	2763.94	3.06
2938	2939.60	-1.60
¹⁷¹ Yb ($I = 1/2$)		
$ g = 2.536, A = 0.0673 \text{ cm}^{-1}$		
2243	2242.75	0.25
2819	2819.54	0.46

orbital angular momentum. The covalency in the Yb³⁺ ion in sites of cubic symmetry has been discussed by Baker (8) and Thornley (9), and comparably large covalency has been observed for the Yb³⁺ ion doped in alkaline earth monoxides CaO and SrO (10) and for Cs₂NaYbCl₆ (11). Smaller g values than the theoretical values due to the covalency effect results in the smaller effective magnetic moment of the Yb³⁺ ion, which is consistent with the experimental results.

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