Single crystal growth and magnetic susceptibility of $Tm_3Al_5O_{12}$

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Abstract

The single crystals of garnet type $Tm_3Al_5O_{12}$ have been successfully grown by a flux method. The magnetic susceptibility was measured over the temperature range of 2.0 to 300 K in a constant magnetic field of 10 kOe. Tm^{3+} ion has an even number of 12-electrons in the $4f$ shell, avoiding the Kramers doublets. The typical Van Vleck paramagnetism has been manifestly observed. The detailed analysis will be presented on the basis of a crystal electric field splitting. It is verified experimentally that the ground state is singlet Γ_2. The value of energy difference between the singlet ground state, Γ_2, and the first excited state, triplet $\Gamma_5^{(2)}$, is estimated to be 68 K.

Key words: $Tm_3Al_5O_{12}$; garnet; Van Vleck paramagnetism; single crystal

1. Introduction

Thulium Aluminum garnet $Tm_3Al_5O_{12}$ has the garnet structure of cubic symmetry of space group $Ia\overline{3}d$ (O_h^{10}) as shown in Fig. 1 [1]. The general chemical formula for an oxide garnet may be written as $\{C\}_3[A]_2(D)_3O_{12}$, with eight of these formula units per unit cell, where the three cation sites are C (dodecahedral)-, A (octahedral)- and D (tetrahedral)-sites in the garnet. These sites are surrounded by oxygen ions O^{2-}. Generally, large ion occupies in order of C-, A- and D-site. Tm^{3+} ions occupy the C-site, Al^{3+} ions occupy the A- and D-sites, where the magnetic ion is only Tm^{3+} ion.

If $g\mu_B\langle 0|J_z|0\rangle = 0$ in the ground state $|0\rangle$, then there is no magnetic effect. However, second order perturbation theory predicts a change in the ground state energy because it takes account of excited states with $\langle s|J_z|s\rangle \neq 0$ being mixed in. The magnetic susceptibility shows the temperature independent behavior at low temperature, known as the Van Vleck paramagnetism. Beautiful and typical Van Vleck paramagnetic suscep-

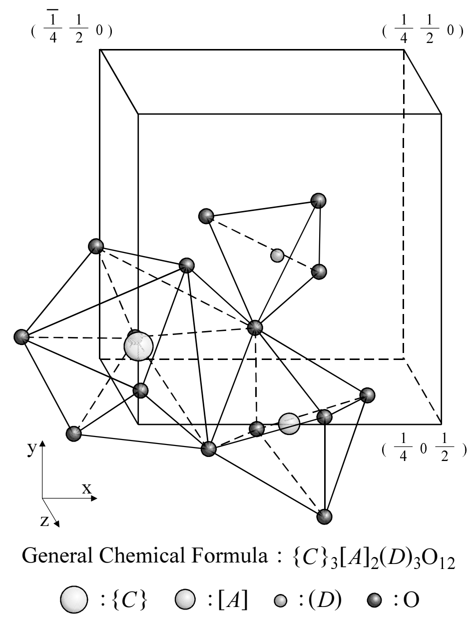

Fig. 1. Garnet structure with the different sites $\{C\}$, $[A]$ and (D).

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tibility has been rarely found. The basic reason is that it is rare to see the ions having the energy level satisfied with some strict conditions [2, 3]. We will present in this paper a typical Van Vleck paramagnetism of $Tm_3Al_5O_{12}$.

2. Experimental methods

A flux method for crystal growth technique was successfully applied to the single crystal growth of $Tm_3Al_5O_{12}$. The starting materials Tm_2O_3 (purity 99.9 %), Al_2O_3 (99.99 %), PbO (99 %) and PbF_2 (98 %) were mixed in the calculated ratio (mol%),

$$Tm_2O_3 : Al_2O_3 : PbO : PbF_2 = 3.9 : 7.0 : 41.5 : 47.6.$$

This initial composition and heating condition were evaluated with a small modification for $Y_3Al_5O_{12}$ [4]. The powder mixture was charged into a 10 ml platinum crucible and the crucible was covered with a cap. The temperature was elevated to 1423 K at the rate of 200 K per hour and was held for 24 hours in a muffle furnace. After completion of the soaking period at 1423 K, the crucible was cooled to 1023 K at the rate of 4 K per hour, then cooled more quickly to room temperature in the furnace. After returning the crucible to room temperature, the crystals were separated from the solidified melts by immersing the crucible in a hot 30 % nitric acid solution around 333 - 353 K for several days.

The d.c. magnetic susceptibility was measured with a Quantum Design superconducting quantum interference device (*rf*-SQUID) magnetometer over the temperature range of 2.0 to 300 K at intervals of approximately 2 K ($2.0 \leq T \leq 120$ K) and 5 K ($120 \leq T \leq 300$ K) in a constant magnetic field of 10 kOe.

3. Results and discussion

The single crystals of $Tm_3Al_5O_{12}$ have successfully grown. The grown crystals have a maximum edge of about 2 - 3 mm in size with shining, light green surface. The lattice constant is $a = 11.960$ Å at room temperature.

Fig. 2 shows the temperature dependence of the magnetic susceptibility of $Tm_3Al_5O_{12}$. The magnetic susceptibility exhibits the temperature independent Van Vleck paramagnetism at low temperature, which verifies the singlet ground state. The magnetic susceptibility decreases monotonically above 120 K without any anomaly. Tm^{3+} ion has an even number of 12-electrons in the $4f$ shell, avoiding the Kramers doublets. The detailed analysis has been made on the assumption that

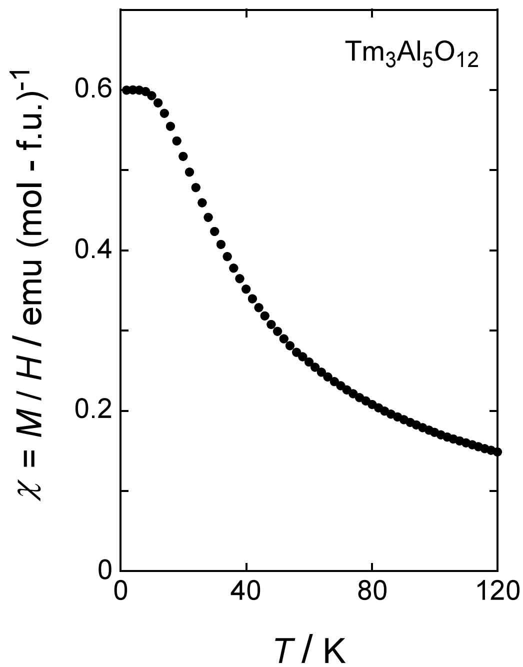

Fig. 2. Magnetic susceptibility of $Tm_3Al_5O_{12}$ per mol formula unit as a function of temperature in a constant magnetic field 10 kOe.

the influence of dominant cubic crystal electric field on $^3H_6$ state with $J = 6$ for Tm^{3+} ion. The Lea, Leask and Wolf theory [5] leads the energy level split of $^3H_6$ multiplet, from the bottom ground state to the highest state to be Γ_2, $\Gamma_5^{(2)}$, Γ_3, Γ_4, $\Gamma_5^{(1)}$ and Γ_1. It is verified experimentally that the ground state is singlet Γ_2. The value of energy difference between the singlet ground state, Γ_2, and the first excited state, triplet $\Gamma_5^{(2)}$, is estimated to be 68 K.

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