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CRYSTAL STRUCTURE OF TbIG IN VARIATION OF TEMPERATURE (298, 150 K) AND MAGNETIC FIELD (H=0, 0.1 T)

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Temperature and magnetic field dependences of crystal structure of TbIG were investigated by X-ray diffraction. Corrections for primary and secondary extinction were made. It was found that temperature variation significantly affects the spherical domain size r, whereas magnetic field affects the mosaic spread η.

Rare earth iron garnets have been extensively studied due to its ferrimagnetism and as materials of microwave device and magnetic bubble memory.[1,2] Recently, we reported asphericity of 4f-electrons in TbIG under 0.1 T of magnetic field at 150 K and 298 K.[3] In order to gain information on magnetic and temperature effects on the domain structure and electron density distribution around Tb^{3+} ion, accurate crystal structures of TbIG without magnetic field at 298 K and 150 K were newly determined this time. Further refinements of absorption and extinction, including primary extinction, were applied to four data sets (298 K, 150 K; H=0, 0.1 T). A drastic change was revealed in the distribution of the electron density around Tb^{3+} ion under H=0 and H=0.1 T. Influence of the magnetic field and temperature on extinction was also observed.

The crystal of terbium iron garnet ($Tb_3Fe_5O_{12}$) is cubic, space group Ia3d and Z=8.[3,4] The Tb^{3+} ion in 24c-site is dodecahedrally coordinated by eight oxygens in 96h-site, the Fe^{3+} ion in 24d-site tetrahedrally by four oxygens and the Fe^{3+} ion in 16a-site octahedrally by six oxygens. Fe in the d-site is antiferromagnetically coupled to Fe in the a-site and to Tb. Net magnetic moment of TbIG gets zero at the compensation point Tc=245 K and above Tc contribution of the Tb ion diminishes and the direction of net magnetic moment changes.

A crystal ground to form a sphere of diameter 0.195(8) mm was used for all the measurements. Reflection data up to ϑ=50° were collected by a Rigaku automated four-circle diffractometer using graphite monochromated Ag Kα radiation. The crystal specimen was cooled by a stream of cold N_2 gas which was surrounded by warm N_2 gas curtain. The crystal was aligned with the [110] direction parallel to the magnetic field of 0.1 T generated by a $SmCo_5$ magnet. Absorption correction was made[5] and the correction for Borrmann effect treated by Zachariasen (1968)[6] was less than 2%, so that it was neglected.

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This crystal is known to suffer severe extinction. Extinction correction based on Zachariasen theory,[7] cited hereafter as Z, is represented as follows.

$$P = P_k y \qquad \text{(Z-46a)},$$

$$y = (1+2p_2\bar{x}_o/p_1)^{-1/2} \qquad \text{(Z-46b)},$$

$$\bar{x}_o = \beta Q_o[\bar{t}+(\bar{T}-\bar{t})/\{1+(\beta/g)^2\}^{1/2}] \qquad \text{(Z-46c)},$$

where P is the integrated intensity of the diffraction beam, P_k is the integrated intensity in the kinematical approximation, y is the extinction factor, Q_o is given by equation (Z-2b) and the p_2/p_1 term is related to the poralization of X-ray. For the spherical domain of radius r, $\bar{t} = \pi r/2$. Introducing angular dependence sin2ϑ mentioned by Becker and Coppens,[8)]

$$\beta = r \sin 2\vartheta/\lambda.$$

Effective mean path length $\bar{T}$ is obtained by the following equation,

$$\bar{T} = [1/A(\mu)] \int (T_1+T_2)\exp[-\mu(T_1+T_2)]d\tau, \text{ [9)]}$$

where A(μ) is the transmission factor and μ is the absorption coefficient. Primary extinction expressed by the term $\beta Q_o\bar{t}$ can not be neglected due to the large domain size $r>10^{-4}$ cm. The refinement was carried out by Program RADIEL[10)] modified to take into account of primary and secondary extinction on the basis of equation (Z-46c) comprising two independent parameters; spherical domain radius r and g which is related to the mosaic spread parameter η by $\eta = 1/2\sqrt{\pi}g = 5.8186/g'$ seconds ($g = g'\text{x}10^4$). Atomic scattering factors were divided into those from the core and valence electrons. Refinements were also carried out for the κ value which describes the expansion-contraction degree and for the population of the valence shell electrons. Atomic scattering factors were taken from International

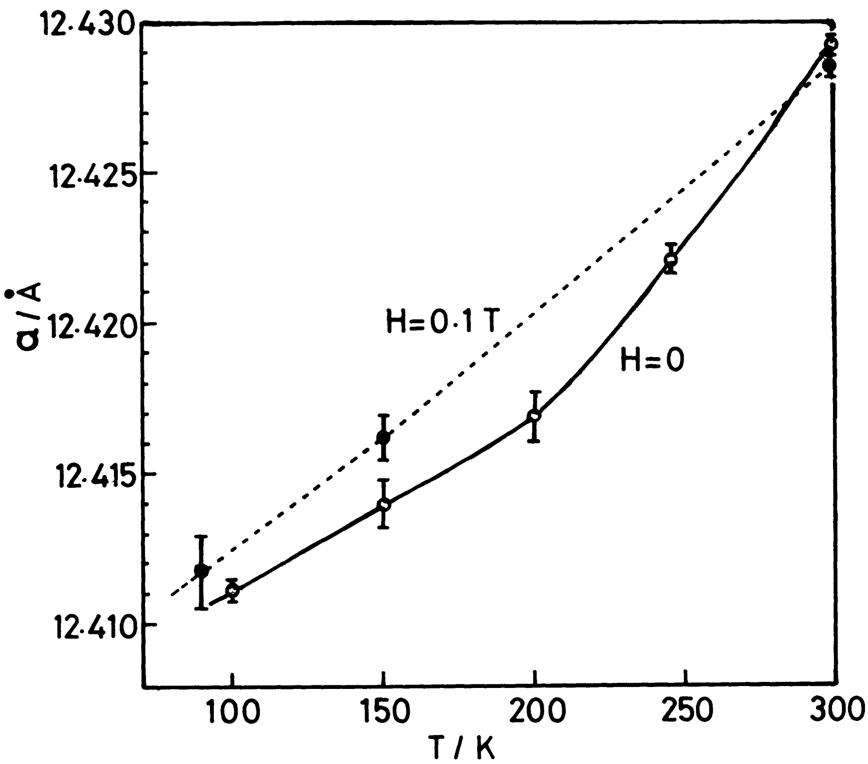


Fig. 1. Temperature dependence of the lattice constant under H=0 and 0.1 T.

Table 1. Spherical domain radius r and mosaic spread parameter η

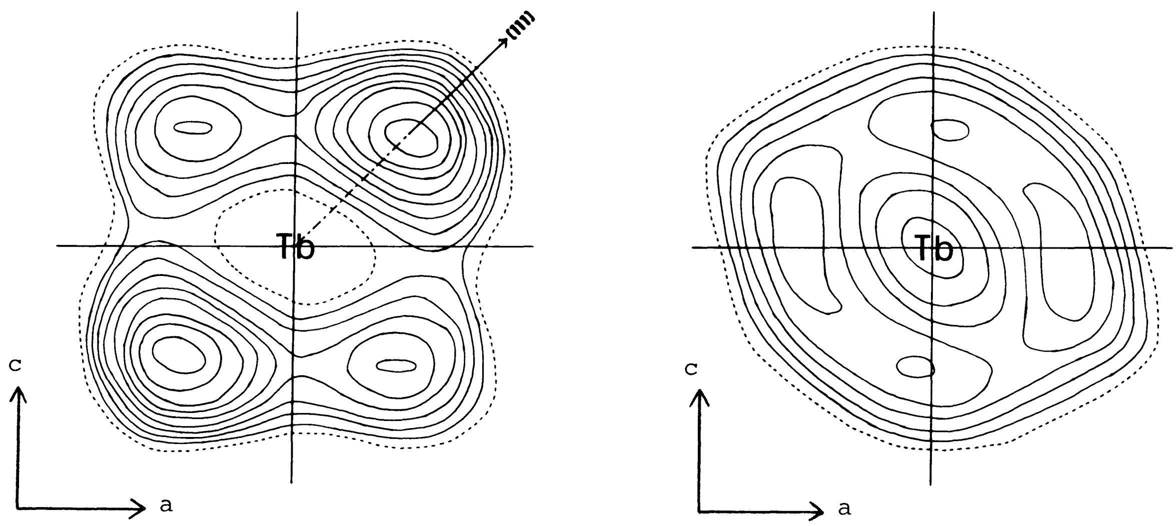
	H = 0		H = 0.1 T	
	298 K	150 K	298 K	150 K
$r/10^{-4}$cm	9.1(5)	6.3(9)	9.4(5)	6.8(12)
η/s	4.1(3)	5.4(6)	3.3(2)	4.4(6)
R(F)	0.026	0.028	0.027	0.031
Rω(F)	0.026	0.028	0.028	0.031

Tables for X-Ray Crystallography IV.[11)]

Temperature dependence of the lattice constant in the absence and presence of a magnetic field (0.1 T) was obtained on the basis of the ϑ values of reflections {16,16,16}, {24,8,8}, {24,8,0}, and {26,4,0} in the range 34°<ϑ<39° (Fig. 1). Under the magnetic field of H=0.1 T, the lattice constant shows linear decrease as the lowering of temperature with the expansion coefficient of 6.58×10^{-6} K^{-1}, whereas without magnetic field there is concavity of $\Delta a/a_o$ vs. T around temperature a little lower than the compensation point, 245 K.

The extinction parameters are given in Table 1. Since the obtained domain size is $>10^{-4}$ cm, the primary extinction can not be neglected. It is evident that temperature significantly affects the domain size r rather than the magnetic field. As for the mosaic spread, η is reduced to about 70% when the magnetic field is applied to the crystal at both temperatures, 298 and 150 K. On the other hand, η appears to increase at lower temperature when the field condition is unchanged. This behaviour seems to depend mainly on the different magnetic structures above and below the compensation point Tc.

Deformation electron-density maps around Tb^{3+} are illustrated in Fig. 2. Eight well-defined peaks 0.41 Å apart from Tb are observed at 150 K and H=0.1 T.



150 K, H=0.1 T 150 K, H=0

Fig. 2. Deformation density maps of the (010) section 0.25 Å below the Tb^{3+} ion at 1/4, 3/8, 1/2.. Contours are at intervals of 0.2 eÅ^{-3}, positive contours are full lines, the zero contours are dotted lines.

Four equivalent peaks along the <111> directions in the $(10\bar{1})$ plane are 1.94 $e\text{Å}^{-3}$ in height and other equivalent peaks along <111> in the (101) plane 1.20 $e\text{Å}^{-3}$. The general feature of the localized electron density under the magnetic field is in good agreement with our previous result[3)] based on the extinction correction of anisotropic Lorentzian type I. Slight difference appeared only in the peak heights which reduced about 20% this time by the correction for primary and isotropic secondary extinction. On the other hand, in the absence of a magnetic field, eight somewhat lower peaks with pseudo-cubic symmetry were observed around Tb ion. They are located in the direction rotated 45° around the axis, passing through Tb and parallel to the b axis, with respect to the peaks under H=0.1 T. Thus, the observation of peaks in the absence of a magnetic field, where magnetostriction is not expected, supports our former interpretation that these peaks are due to asphericity of 4f-electrons. When the magnetic field was applied, the localization of 4f-electrons was observed in the direction of easy axis <111> to which magnetization is bound. The deformation density at 298 K differed entirely from that at 150 K, which can not be interpretated at this stage. The discussion in detail will be reported later elsewhere.

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