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DETERMINATION OF THE SPECIFIC SITE OCCUPATION OF RARE EARTH
ADDITIONS IN $\text{Y}_{1.7}\text{Sm}_{0.6}\text{Lu}_{0.7}\text{Fe}_5\text{O}_{12}$ THIN FILMS BY THE ORIENTATION
DEPENDENCE OF CHARACTERISTIC X-RAY EMISSIONS

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ABSTRACT

The orientation dependence of characteristic x-ray emissions have been used to determine specific site occupations of Rare Earth additions in epitaxially grown films of $\text{Y}_{1.7}\text{Sm}_{0.6}\text{Lu}_{0.7}\text{Fe}_5\text{O}_{12}$. A theoretical formulation based on the assumption of highly localized inner shell excitations was used not only to predict specific site sensitive orientations, but also to refine experimentally observed data employing a constrained least squares analysis to give probabilities for the occupation of the RE additions in the different crystallographic sites. Thus, it has been shown that in this compound the preference for the RE additions is a predominantly octahedral occupation with a probability $\geq 95\%$. Some of the assumptions and limitations of the technique have also been discussed.

INTRODUCTION

The uniaxial magnetic anisotropy in epitaxially grown garnet films consists of a growth-induced component and a stress-induced component. The latter component arises due to magneto-elastic interactions [1]. The former component, as the name implies, originates from the growth process and is explained in terms of the presently accepted "site preference" model [2,3,4]. According to this model the uniaxial anisotropy is attributed to the preferential occupation of the Rare Earth (RE) elements in the different crystallographic sites of the garnet lattice. But the results obtained by different investigators [5,6] using this model for the RE occupations are controversial, if not contradictory. However, it has been observed that there is an order of magnitude reduction and subsequently, ultimate loss of the value of the anisotropy constant (K_u) on annealing [7]. This observation is an indirect proof for the site preference model of anisotropy, but specifically which sites are involved is unclear [8].

Traditionally, this cation distribution problem has been experimentally investigated by one of the following methods: (1) Magnetization; (2) Magnetic Aniso-

trophy; (3) Optical Spectroscopy; (4) Mössbauer Spectroscopy and (5) Spin Echo (see Ref. [9] for a detailed review). These techniques are limited in their application to bulk samples and hence can resolve average distribution only. Here we present an alternative technique for the evaluation of specific site occupancies of RE substitutions in $Y_3Fe_5O_{12}$ (YIG) based on the orientation dependence of electron-induced characteristic x-ray emissions. The advantage of this technique over the ones mentioned earlier is that a converged electron probe is used and hence local areas of the sample can be studied. Ideally, this should allow us to determine RE distributions as a function of the non-equilibrium growth process, by studying sequential slices of thin films.

THE TECHNIQUE: PHYSICAL DESCRIPTION

As a result of the dynamical scattering of an incident plane wave of high energy electrons, a standing wave pattern is set up within the crystal unit cell [10]. This intensity modulation within the crystal is dependent on the incident beam orientation and under favorable conditions will be a maximum on certain crystallographic sites. Hence, highly localized scattering events, like inner shell excitations, show a strong orientation dependence [11,12]. Further, it has been shown that for certain systematic or "planar channelling" conditions, the characteristic x-ray emissions induced by the channelling or blocking of the incident electrons, can provide information on the occupancy of specific crystallographic sites by different elements, provided that an a priori knowledge of the distribution of some reference elements is available [13,14,15]. This is particularly applicable for crystals with a layered structure (i.e. crystals that in some crystallographic projection can be resolved into alternating layers of parallel non-identical planes [A,B,A,B,...], where the appropriate systematic orientation can be determined by mere inspection. For example, the spinel structure compounds can be resolved in

the [001] projection into alternating planes of tetrahedral and octahedral sites and hence a $\bar{g} = 400$ systematic orientation can be easily seen to be appropriate for this kind of experiment. The garnet structure on the other hand, is more complicated and a number of crystallographic projections calculated using the ORTEP [16] program failed to indicate a systematic orientation that could be specific site sensitive. As a result, the electron induced characteristic x-ray intensities for different orientations and different site occupations have to be calculated in order to determine the appropriate systematic or "planar channelling" condition suitable to study site occupations for this particular crystal structure.

THEORETICAL FORMULATION

Assume that the electron-induced characteristic x-ray emission of an element 'q' at the coordinate $\bar{\rho}$ in the unit cell is proportional to the intensity of the electron standing wave at $\bar{\rho}$ and the probability of the localization of the standing wave at $\bar{\rho}$, $P(\bar{\rho})$. It is reasonable [17] to assume that $P(\bar{\rho})$ is highly localized, i.e. a delta function at the mean atomic positions. Hence, for a crystal of thickness 't'

$$N_q = \sum_{RSI} \int_0^t \Phi^* \Phi dz$$

where N_q is the intensity of the characteristic x-ray emission of element q and the summation is over the appropriate crystallographic sites of interest in the unit cell. Φ is the amplitude of the scattered wave at any depth z expressed as a linear combination of Bloch waves (for an incident plane wave) in the conventional dynamical theory formulation [10].

On carrying out the integration and rearranging the different terms, the characteristic x-ray intensity per unit thickness can be expressed as

$$N_q = \sum_{\mathbf{g}, \mathbf{h}} \left[\sum_{\mathbf{j}, \mathbf{l}} \exp((\mathbf{h} - \mathbf{g}) \cdot \mathbf{x}) \left\{ \sum_{\mathbf{j}=1} \left[C_o^{(\mathbf{j})} C_g^{(\mathbf{j})} C_o^{(\mathbf{l})} C_h^{(\mathbf{l})} \right. \right. \right. \\ \left. \left. + \sum_{\mathbf{j}, \mathbf{l}} C_o^{(\mathbf{j})} C_g^{(\mathbf{j})} C_o^{(\mathbf{l})} C_h^{(\mathbf{l})} \frac{\sin[(k_z^{(\mathbf{j})} - k_z^{(\mathbf{l})})t]}{(k_z^{(\mathbf{j})} - k_z^{(\mathbf{l})})t} \right\} \right]$$

where $C_o^{(\mathbf{j})}$ are Bloch wave coefficients and $k_z^{(\mathbf{j})}$ are components of the wave vector for the electrons in the crystal.

CALCULATIONS

The electron induced characteristic x-ray emission intensities were computed using the above expression for MgAl_2O_4 , a compound with the spinel structure. A 15-beam, $\bar{g} = 400$ systematic excitation condition was chosen and the calculated intensities at an acceleration voltage of 100kV were found to be in agreement with experimental results [18]. This served as a verification for the validity of the theoretical formulation.

X-ray emission intensities were then calculated for complete RE occupation in any one of the three crystallographic sites of the prototype compound YIG for different systematic excitation conditions (i.e. $\bar{g} = 00\bar{2}$; $\bar{g} = \bar{2}20$; $\bar{g} = 1\bar{2}1$, etc.) to determine an orientation with specific site sensitive characteristic x-ray emission. These 11-beam calculations were performed for a range of crystal thicknesses ($250\text{\AA} - 2000\text{\AA}$) and for a range of specimen tilts ($0 < k_x/g < 2$). The x-ray production was found to be insensitive to crystallographic orientation for excitation of the ($\bar{g} = 002$) and ($\bar{g} = \bar{2}20$) systematic conditions. On the other hand strong orientation dependence for the ($\bar{g} = 1\bar{2}1$) systematic excitation were observed at the first order Bragg diffraction condition ($k_x/g = 0.5$) and for negative and positive excitation errors (Fig. 1), i.e. channeling for dodecahedral site substitution of RE additions; blocking for tetrahedral site substitutions and an insensitivity to orientation for octahedral site substitutions.

EXPERIMENTAL DETAILS AND RESULTS

Samples of nominal melt composition $\text{Y}_{1.7}\text{Sm}_{0.6}\text{Cu}_{0.7}\text{Fe}_5\text{O}_{12}$, $0.94\mu\text{m}$ thick, prepared by liquid phase epitaxy on GGG substrates at a growth temperature of 969°C and a growth rate of $1.76\mu\text{m}/\text{min}$ were studied. Details of the preparation of these samples are given elsewhere [19]. Thin foils of these samples for TEM studies were prepared by the ion-milling technique.

Experiments were performed on a Philips 400 ST analytical TEM fitted with a LaB_6 filament and an energy dispersive x-ray analyzer. A low background double tilt holder to reduce x-ray background intensities was used in all experiments. Stray x-ray generation was further minimized by using gridless self-supporting specimens. The specimen thickness was estimated to be approximately $500\text{\AA}$. The incident beam divergence was a few milliradians and the probe diameter was $500\text{--}1000\text{\AA}$. The latter is determined by the level of contamination and the actual counting time. The characteristic x-ray emissions were collected at different orientations of the collimated electron beam based on the calculations described earlier. A strong $[\bar{1}21]$ systematic row was excited and spectra acquired at six different values of the specimen tilt described by the parameter: $k_x/g \approx 0, 0.375, 0.5, 0.875, 1.00$ and 1.125 where k_x/g is defined such that $k_x/g = 0.5$ for the first order Bragg diffraction condition. The specimens were oriented using convergent beam electron diffraction patterns.

In order to ensure proper statistics, spectra were collected (at the appropriate orientations) for a total counting time of 600 seconds and a counting rate of ~ 3000 counts/sec. A hole count was taken at periodic intervals and subtracted along with the continuous background from the spectra. Because of the large counting time (600 secs) and the susceptibility of the specimen to damage and contamination, the spectra was collected at a different specimen sampling area at each specimen tilt. Care was taken to ensure that the specimen thickness was not

significantly different for different acquisitions. However, small differences in counting rates or changes due to the small displacement of the probe have to be incorporated in the analysis. This was done by scaling the integrated elemental intensities using normalized values of the total integrated intensities of the whole spectra.

The scaled integrated intensity for the two RE additions are shown in Table 1. The standard deviations of the observations are approximately 0.5% and 0.65% for $\text{Lu}(\text{L}_\alpha)$ and $\text{Sm}(\text{L}_\alpha)$ respectively.

TABLE 1. Characteristic x-ray intensities (normalized)

K_x/g	0	0.375	0.5	0.875	1.0	1.125
$\text{Lu}(\text{L}_\alpha)$	50807	49747	49130	50142	48985	50437
$\text{Sm}(\text{L}_\alpha)$	31911	31754	31808	32073	31218	31805

ANALYSIS

The results (Table 1) are statistically significant, but a clear agreement with the theoretical predictions is not obviously evident. This is interpreted as being due to a mixed distribution of the RE elements in all three possible crystallographic sites. The probabilities of the distributions can then be determined by a least squares analysis, based on the algorithm of constrained least squares by Lawson and Hanson [20].

An error term is defined here as the difference between the experimentally observed intensity and an intensity calculated as a summation over all sites of the product of the theoretical value for complete occupation of each site (calculated earlier) and a weight factor representing the probability of occupation of that specific site. For each element of interest, i.e. Sm and Lu, a summation over all orientation of the square of this error term is minimized, subject to the constraint

that all the weights are positive [21]. The results of the least squares refinement for the weights of the occupation for each element in a particular site is shown in Table 2.

TABLE 2. Relative weights for the site occupancy of Rare Earth additions

	Octahedral	Tetrahedral	Dodecahedral
Lu	0.2141 $\pm$ 0.02	0.0049 $\pm$ 0.0005	**
Sm	0.1679 $\pm$ 0.0164	**	0.0095 $\pm$ 0.0007

DISCUSSION

A significant though reasonable assumption in this experimental technique is that the x-ray emission process is highly localized, i.e. it can be approximated by a delta function at the mean atomic positions. Based on band structure calculations, the inner shell radii have been estimated [22] to be of the order of 0.02 $\text{\AA}$. Further, Bourdillon *et al.* [16] have shown complete localizations for all excitation energies within the detectability limits of conventional energy dispersive x-ray detectors. Further, reductions in the orientation-dependent x-ray emission intensities for temperature rises up to 200°C has been shown [11] to be insignificant when compared with reductions due to angular spread, based on computations for a range of Debye-Waller factors. These arguments bear out the assumption.

It is acknowledged that the present approach neglects absorption effects in the crystal and the fact that a convergent probe as opposed to parallel illumination was used in the experiment. A more rigorous formulation would have to include these in the analysis. However, the latter could easily be accommodated by re-doing the calculations for a whole range of incident orientations and incorporating these values in the least squares refinement.

Within the limitations of the assumptions of the technique, it can be inferred that the RE substitution in the octahedral sites for this compound are highly probable (~95%). These results are in good agreement with earlier studies [23,24] particularly for the distribution of the small rare-earth ion Lu^{3+} which can be easily accommodated in the smaller octahedral sites. A determination of the contribution of these ions to the magnetic anisotropy demands the exact knowledge of the valence state of the cation in addition to the site occupancy and is beyond the scope of this work.

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Figure 1

FIG. 1. Variation of electron-induced characteristic x-ray emission with orientation for a garnet structure. These calculations were carried out for an $11\bar{1}$ -beam, $g = 1\bar{2}1$ systematic row and for a range of incident beam orientations ($0 \leq k_x/g < 1.0$).

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