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Antisite Defects in Yttrium Iron Garnet


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Abstract. NMR of \(^{57}\)Fe nuclei is used to study the \(\bar{Y}\) antisite defects (yttrium ions on the sites nominally occupied by iron) in yttrium-iron garnet (YIG). In spectra of both tetrahedral and octahedral Fe\(^{3+}\) ions, satellite lines appear, corresponding to Fe\(^{3+}\) ions with this defect in their vicinity. NMR was measured on a number of nominally pure YIG samples - single crystals, thin films as well as polycrystalline samples. The content \(x_f\) per formula unit of the \(\bar{Y}\) antisite defect \((Y_f)\) was determined from the amplitude of the satellite lines and it lies in the interval 0.001 < \(x_f\) < 0.03. In most cases the satellite lines caused by the \(Y_f\) defect are obscured by the satellites originating from other impurities. In high purity single crystals the satellites caused by \(Y_f\) dominate, however. In the NMR spectra of these single crystals the satellite lines which correspond to the Fe\(^{3+}\) ions in seven different crystallographically inequivalent positions with respect to the defect are resolved at low temperatures. Further unresolved satellites emerge from the main lines as the temperature is increased.

1. INTRODUCTION

In an ideal yttrium-iron garnet with the chemical formula \(Y_3Fe_5O_{12}\), the dodecahedral (c) sites are occupied by the \(Y^{3+}\) ions only, while octahedral (a) and tetrahedral (d) sites are completely filled by the Fe\(^{3+}\) ions. In real YIG systems a small amount of the cations may be misplaced - ferric ions may enter the c sites (Fe antisite defect), while the \(Y^{3+}\) ions may appear on the a sites \((Y_a - Y\) antisite defect). Because of relatively large ionic radius of the \(Y^{3+}\) ion it is improbable that this ion will appear on rather small d sites.

To study the antisite defects experimentally is a difficult task. Most methods (like measurements of the magnetic moment or the magnetocrystalline anisotropy, ferromagnetic resonance etc.) give information about the system as a whole and it is not easy to find out the role of a specific defect, especially when more types of defects are present. Nuclear methods on the other hand provide information concerning the local properties and could therefore be used to characterize the defect, provided the sensitivity and resolution of the method in question is sufficient. NMR of the \(^{57}\)Fe nuclei measured by the spin echo method is a suitable tool for such a study. Due to the change of the hyperfine field caused by the defect, the NMR frequency of the \(^{57}\)Fe nuclei which are situated near the defect is shifted with respect to the frequency of the nuclei in an ideal environment. If the shift is larger than the linewidth of the NMR line, a resolved satellite line appears.

We first reported the detection of satellites caused by the \(Y_f\) defect in [1]. In [2] NMR of the \(^{57}\)Fe nuclei in a high purity YIG single crystal was analysed. In this case more than twenty satellite lines were detected, which all correspond to the \(Y_f\) defect in different relative positions with respect to the resonating nuclei.

1.1 Satellite lines caused by the \(Y_f\) defect

The overall pattern of the satellites follows from the symmetry of the problem and it was discussed in some details in [2]. For magnetization along the easy <111> direction the \(^{57}\)Fe NMR spectrum consists of three main lines and a number of groups of satellite lines. The main line \(d\) \((f_m \approx 64\) MHz at \(T=4.2\) K) corresponds to the ferric ions on the tetrahedral sublattice, while Fe\(^{3+}\) ions on the octahedral sites give rise to lines \(a\) \((f_m \approx 75\) MHz) and \(c\) \((f_m \approx 76\) MHz). With the exception discussed below the amplitudes of the satellite lines are the same and the satellites are grouped into sets, each set containing four satellite lines. These sets correspond to the sets of the crystallographically equivalent configurations (CEC) of the pair \((Y_f\) defect - Fe\(^{3+}\) ion). The frequencies of the satellites belonging to the same CEC set differ only because the hyperfine field is anisotropic. The satellites corresponding to one CEC set can be identified since the temperature dependence of their resonance frequencies is to a good approximation the same [2].

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The exception mentioned above corresponds to the case when the Fe$^{3+}$ ion is on the octahedral site and it lies on the same body diagonal as the Y$_s$ defect, moreover the body diagonal coincides with the local trigonal symmetry axis. In this case the (Y$_s$ defect - Fe$^{3+}$ ion) pairs still posses a local trigonal symmetry and the corresponding CEC set gives rise to a characteristic pattern of two satellite lines - the satellite belonging to the $a_t$ line has the same amplitude as all satellites discussed above, but the satellite belonging to the $a_s$ line has the amplitude three times smaller.

If we assume that the distribution of the defects in the system is random, the shapes of the main and satellite lines are the same and the ratio of the amplitudes of satellite and corresponding main line is given by:

$$I_{sat}/I_{main} = n.c/(1-c)$$

where $c$ is the concentration of the defect, $n$ is the number of magnetically equivalent configurations of the defect and the resonating nuclei. For $M$ along the $<111>$ direction $n$ is equal to 1, 6 and 2 for satellites belonging to the $a_t$, $a_s$ and $a_l$ lines, respectively. Note that the concentration of the defect may be determined easily from the above relation, with no need for an external standard.

The change of the frequency i.e. the splitting between the satellite and the corresponding main line depends on the relative position of the defect and the resonating nuclei and on the direction of the magnetization. It is determined by the microscopic mechanisms - by the change of the dipolar field (the magnetic Fe$^{3+}$ ion is substituted by a nonmagnetic Y$^{3+}$ ion) and by the changes of transferred and supertransferred interactions. These are similar, though not identical, with the mechanisms of the superexchange interaction. The isotropic part of the splitting is equal to the average of the splittings for satellites in the CEC set [2].

2. EXPERIMENTAL

During the last ten years we studied NMR of $^{57}$Fe in a number of YIG systems containing different substitutions and defects (see [1-4] and references therein). In all these compounds we found that the width of NMR lines is determined by the inhomogeneous broadening i.e. by unresolved satellite lines caused by the defects and impurities. In imperfect systems with high content of impurities the NMR lines are thus broad and only few - if any - satellite lines are resolved. This is the reason why the satellite lines caused by the Y$_s$ defect are observed in relatively pure YIG systems only. On the other hand they are present in systems prepared by diverse methods - single crystals as well as thin films and polycrystalline samples. In Table I we give characteristics of several representative YIG systems in which the Y$_s$ satellites were detected.

Table I. Representative systems in which the satellite lines caused by the Y$_s$ defect were detected. $x_y$ is the content of the Y$_s$ defect per formula unit determined from the relative intensity of the satellite. All thin films were grown using the LPE method on [111] oriented GGG substrates. Content (per formula unit) of impurities with the highest concentration is also given.

<table>
<thead>
<tr>
<th>system</th>
<th>characteristics</th>
<th>$x_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>single crystal grown from the BaO/B$_2$O$<em>3$ flux, $x</em>{Si} \approx 0.006$</td>
<td>0.015(2)</td>
</tr>
<tr>
<td>S2</td>
<td>single crystal obtained by the floating zone method</td>
<td>0.030(2)</td>
</tr>
<tr>
<td>S3</td>
<td>single crystal YIG:Si, PbO/PbF$_2$/B$_2$O$<em>3$ flux, $x</em>{Si} = 0.027$</td>
<td>0.0010(3)</td>
</tr>
<tr>
<td>P1</td>
<td>polycrystal obtained by the standard ceramic technology, $x_{si} \approx 0.006$</td>
<td>0.0030(4)</td>
</tr>
<tr>
<td>P2</td>
<td>polycrystal obtained by the spray drying method, $x_{Mn} \approx 0.001$</td>
<td>0.0030(4)</td>
</tr>
<tr>
<td>F1</td>
<td>thin film, PbO/B$<em>2$O$<em>3$ flux, platinum crucible, $x</em>{pb} \approx 0.009$, $x</em>{p} \approx 0.009$</td>
<td>0.008(1)</td>
</tr>
<tr>
<td>F2</td>
<td>thin film, PbO/B$_2$O$<em>3$ flux, gold crucible, $x</em>{pb} \approx 0.012$</td>
<td>0.004(1)</td>
</tr>
<tr>
<td>F3</td>
<td>thin film, BaO/B$_2$O$<em>3$ flux, platinum crucible, $x</em>{pb} \approx 0.004$</td>
<td>0.008(2)</td>
</tr>
</tbody>
</table>

The NMR spectra were measured by the spin-echo method using a phase-coherent spectrometer with averaging technique and complex Fourier transformation. The rf power was adjusted to excite the nuclei inside the domains only. For most of the samples the longitudinal relaxation time $T_1$ is rather long, ranging from 0.1 to more than 30 s at $T=4.2$ K. Averaging (up to 10000 times), which is necessary to improve the signal/noise ration and to observe weak satellite lines, is then a time consuming procedure. In these cases a Carr-Purcell sequence of pulses [5] was used, which allowed to shorten the time of measurement significantly [4]. Most measurements were performed in zero external magnetic field i.e. with the magnetization along the easy $<111>$ direction and at liquid helium or liquid nitrogen temperatures. For the single crystal S1, however, the angular dependence at 4.2 K as well as the temperature dependence in the zero external field were measured too [2], [6].
3. RESULTS AND DISCUSSION

The NMR spectra of $^{57}$Fe nuclei in the single crystals S1 and S2 are displayed in Fig. 1. The decomposition of the spectrum on the satellite lines is indicated and the satellites are labelled ($s_i$ denotes j-th satellite from the i-th CEC set, the CEC sets are ordered according to the increasing $Y_i$-$Fe^{3+}$ distance). The problem of determination to which CEC set given satellite belongs was solved in [2] by analysing the temperature dependence of the splittings between the satellites and corresponding main lines. The correctness of this identification was confirmed recently by measuring the angular dependence of the NMR [6].

![Fig. 1. NMR spectrum of the $^{57}$Fe nuclei in two YIG single crystals (S1, S2 in Table I) at the liquid helium temperature. To see clearly the satellite structure, the spectra magnified 20x for the d line and 10x for the a lines are also shown. Dashed and dotted curves in the magnified spectra correspond to S1 and S2 single crystals, respectively. The amplitudes of d and a, lines were separately adjusted to 100. Vertical bars denote the position of the satellites.](image)

It is seen from Fig. 1 that in agreement with the discussion in §1.1 the amplitudes of the satellites are the same with the exception of satellites $s_{11}$ and $s_{111}$ which are three times less intensive. Of particular interest are satellites $s_{11}$ ($i=1,2$). They correspond to the 21st CEC set in which the $Y_i$ defect and the iron nuclei are 1.072 nm apart. The fact that they are resolved indicates the long range of the hyperfine field modification caused by the defect [2].

As documented in Table I, we have found the satellites caused by the $Y_i$ defects in all YIG systems, which exhibit the necessary prerequisite of narrow NMR lines. Up to now about forty such systems - single crystals, polycrystalline samples and thin films were studied. The content $x_i$ (per formula unit) of the $Y_i$ defect was found to lie in the range $0.001 < x_i < 0.03$. $x_i$ presumably depends on the temperature at which the system is prepared and on the way it is annealed, but no systematic study in this direction was attempted until now.

$Y_i$ defect is nonmagnetic and it substitutes Fe$^{3+}$ ion on the a site. As the magnetic moment of this Fe$^{3+}$ ion is antiparallel to the total magnetic moment, the presence of $Y_i$ defects increases the magnitude of the magnetization [7] - corresponding increase per formula unit $5x_i\mu_B$ (at 0 K) may explain why the magnetic moment at 0 K of nominally pure YIG is found to be larger than $5\mu_B$ as a rule.

We now turn to another interesting result we obtained when studying the high purity YIG systems, namely to the temperature dependence of the shape of the NMR lines. At low temperatures the lines are to a good approximation symmetrical. With increasing temperature a strong asymmetry develops, which has similar character for all lines - a tail on the low frequency side of the lines appears. As examples, the temperature dependences of the $a$ and $d$ lines are displayed for the $S1$ single crystal in Figs. 2, 3. The magnitude of the asymmetry is proportional to the content of the $Y_i$ defect. This may be seen from Figs. 2, 3, where the NMR lines of the S2 single crystal at $T=230$ K are also shown - $x_i$ in S2 is approx. two times larger than $x_i$ in S1 (Table I), the asymmetry exhibits similar ratio, if we take into account that measurement on S2 system was performed at slightly higher temperature than the measurement on S1.

The asymmetry may be explained if we take into account the change of the Fe$^{3+}$ molecular field, which is caused by the $Y_i$ defect. Such a change would lead to a different temperature dependence of the magnetic moments of Fe$^{3+}$ ions in the vicinity of the defect, which in turn results in a different temperature dependence of corresponding hyperfine fields. The change of the molecular field arises from two sources:

(i) direct modification of the exchange interactions by the presence of the defect. Clearly this modification is the largest for the nearest $d$ neighbours of the defect, for which one of the four exchange bonds disappears. However, the modification has
surprisingly long range as indicated by our observation of resolved NMR satellites corresponding to the Fe\(^{3+}\) ions in the distance bigger than 1 nm. It is not clear, however, why such modification should have the same character for the prevailing number of the Fe\(^{3+}\) - defect pairs.

(ii) Indirect modification - as the molecular field on the nearest Fe\(^{3+}\) neighbors of \(Y\), is weaker, their magnetic moments will be smaller at elevated temperatures comparing to the moment of Fe\(^{3+}\) ions in an ideal environment. As a consequence the molecular field on the neighbors of such Fe\(^{3+}\) ions will be reduced. With increasing temperature the reduction of the molecular field will affect more and more distant Fe\(^{3+}\) ions. The fact that the asymmetry has similar character for all the lines indicates that it is the indirect modification of the molecular field which prevails.

We performed a decomposition of the low frequency tail of the main lines, assuming that it is caused by unresolved satellites connected with the \(Y\), presence. To explain the asymmetry at 200 K we have to assume that 120 - 170 Fe\(^{3+}\) neighbours are affected (this corresponds to a radius of the interaction about 1.2 nm).

Interestingly fact is that while the presence of the yttrium antisite defects in YIG is now well established, we found no evidence for the presence of any other intrinsic defect. In particular no satellites which would correspond to iron antisite defects (iron on the c sites) \[S\], oxygen vacancies, or the Fe\(^{3+}\) ions were observed. Note that the present sensitivity of the NMR measurement allows to detect satellites which correspond to the defect concentration as low as 0.05 %. Our measurements therefore indicate that the content per formula unit of the simple iron antisite defect (Fe\(^{3+}\) ion on the c sites) is smaller than 0.0015. On the other hand we can not exclude that above listed intrinsic defects form more complex composites (e.g. one or two Fe\(^{3+}\) ions on either c or a sublattice attached to an oxygen vacancy). Satellite structure arising from such 'composite' defects will be more complex and satellite lines will be less intensive comparing to the satellites caused by the isolated point defects. As a consequence, despite the high sensitivity of the NMR measurements, these defects could still escape our attention.

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**References**