Giant polarization and magnetic dynamics in GdMn$_2$O$_5$

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Abstract. Polarization, dielectric permittivity, and low-frequency magnetic dynamics (30 - 50 GHz) of GdMn$_2$O$_5$ are presented. The emergence of an abnormally high polarization along the b axis reported recently by N. Lee et al. is verified. It is found that this polarization is rigid and is observed in the internal field. Superlattices formed due to phase separation and charge carrier self-organization in the bulk of GdMn$_2$O$_5$ the single crystals are revealed. The superlattices manifest themselves in the form of a set of ferromagnetic resonances which are responses of individual superlattice layers. A weak polarization along the c axis at T≤ 130 K caused by the superlattices is observed. The superlattices that occupy a small crystal volume are likely to be domain walls of the rigid bulk multiferroic domains. The correlation between magnetic structure, magnetic dynamics, and polarization in GdMn$_2$O$_5$ is analyzed.

1. Introduction
Orthorhombic manganites RMn$_2$O$_5$ (R – rare earth ion) [1, 2] are examples of multiferroics in which ferroelectricity occurs at the same temperature as a special type of magnetic ordering and is driven by it. These multiferroics are characterized by a strong magnetoelectric effect. The possibility to control electric (magnetic) properties by applying a magnetic (electric) field attracts considerable attention to these materials.

The polar order along the b axis in RMn$_2$O$_5$ occurs due to charge and magnetic orderings. Non-centrosymmetric ion positions in the lattice and polarization in RMn$_2$O$_5$ result from the exchange striction mechanism [3]. The polarization is typically of the order of 0.03 - 0.05 $\mu$C/cm$^2$ [2]. The polar and magnetic ordering temperatures in RMn$_2$O$_5$ are $T_C \approx 35$ K and $T_N \approx 40$ K, respectively.

Among RMn$_2$O$_5$, GdMn$_2$O$_5$ is of special interest. Recently, an observation of the abnormally high polarization along the b axis in GdMn$_2$O$_5$ ($P_b = 0.36$ $\mu$C/cm$^2$) was reported [4]. This is very unusual because a complicated magnetic structure (incommensurate and spiral structure) typically

![Figure 1. AFMR of the Mn-subsystem and ferromagnetic resonance of the Gd-subsystem (T = 5K) [6].](image-url)
induces a much lower polarization in multiferroics of this family. The Gd-Mn symmetric exchange
striction plays a major role in the polarization of GdMn$_2$O$_5$ [4].

As the x-ray resonance magnetic scattering study has shown [4], GdMn$_2$O$_5$ is characterized by a
uniform antiferromagnetic structure with the wave vector $\mathbf{q} = [1/2, 0, 0]$. In this case, the magnetic
order parameter contributes to both the Mn and Gd ions which are interrelated by a strong exchange
interaction. Thus, the homogeneous magnetic structure of GdMn$_2$O$_5$ leads to an abnormally strong
polarization. This paper is concerned with further studies of the magnetic structure and polarization
features in GdMn$_2$O$_5$.

Note that earlier magnetic dynamics (antiferromagnetic resonances (AFMR) and mixed magneto-
electric modes) studies also revealed unusual excitation spectra in GdMn$_2$O$_5$ and its magnetic
structure. Comparison of NRMS and RMS has shown that, along with this ordered state, some Gd ions
occurred. Two branches of resonance excitations were observed. One of them, with a gap near 150 GHz, was typical of AFMR
for the uniaxial collinear antiferromagnetic without a weak ferromagnetic moment. The second branch
with the gap near 110 GHz was caused by the paramagnetic Gd subsystem magnetized by the Mn
subsystem (Fig.1). Thus, the magnetic dynamics spectra observed in [5, 6] were consistent with the
magnetic structure observed in x-ray resonance magnetic scattering in [4].

In this paper we consider polarization, dielectric properties, and low-frequency magnetic dynamics
(30 – 50 GHz) of GdMn$_2$O$_5$. We confirm the existence of a high polarization in GdMn$_2$O$_5$ oriented
along the b axis and study its properties. Specific features of GdMn$_2$O$_5$ magnetic state resulting from
the ground state of the Gd$^{3+}$ ion ($^6S_{7/2}$) and the Gd-Mn exchange interaction are analyzed. A set of
ferromagnetic resonances (FMRs) in the frequency range (30 – 50 GHz) similar to that observed
earlier for other RMn$_2$O$_5$ is revealed in GdMn$_2$O$_5$ [7, 8]. Like in [7, 8, 9], we attribute the set of FMRs
to individual superlattice layers formed in the GdMn$_2$O$_5$ bulk due to phase separation and charge
carrier self-organization.

2. Specific features of magnetic structure of GdMn$_2$O$_5$

All ions in RMn$_2$O$_5$ are in the layers perpendicular to the c axis [10]. The unit cell of RMn$_2$O$_5$ includes
two manganese ions. They are Mn$^{3+}$ ion and Mn$^{4+}$ ion with ($3t_{2g}$ $1e_g$) and ($3t_{2g}$ $0e_g$) 3d electron states,
respectively. Mn$^{3+}$ ions occupy positions $z = 0.25$ c and (1−$z$) = 0.75 c in the octahedral oxygen
environment (MnO$_6$); Mn$^{4+}$ ions are in positions $z = 0.5$−c and have the environment in the form of a
pentagonal pyramid (MnO$_5$); R$^{3+}$ ions occupy positions z=0 c.

Since the polarization in RMn$_2$O$_5$ is typically induced by a special type of magnetic ordering, the
unusual properties of the polar order in GdMn$_2$O$_5$ should be sought for in specific features of its
magnetic structure.

Because of a strong absorption of neutrons by Gd ions an information on the magnetic structures
of the Mn and Gd ion subsystems of GdMn$_2$O$_5$ can be obtained by the x-ray magnetic scattering
technique [4] and from magnetic dynamics spectra [5, 6]. X-ray magnetic scattering in off-resonance
(NRMS) and at the Gd L$_3$-edge (resonance – RMS) conditions in GdMn$_2$O$_5$ [4] have shown that both
magnetic subsystems (Mn and Gd ions) are highly interrelated and form a common order parameter.
An incommensurate magnetic structure with wave vector $\mathbf{q} = (0.49, 0,
0.18)$ arises in the temperature range $T_{N1} = 33$ K – $T_{N2} = 30$ K. Near $T_{N2}$ a lock-in transition into a
commensurate magnetic phase with wave vector $\mathbf{q} = (1/2, 0, 0)$ which extends to the lowest temperatures
occurs. Comparison of NRMS and RMS has shown that, along with this ordered state, some Gd ions
which are in the paramagnetic state exists [4].

Note that the AFMR branch typical of the uniaxial antiferromagnetic collinear structure along the a
axis observed for GdMn$_2$O$_5$ [5, 6] most likely originated from the antiferromagnetic Gd-Mn order
parameter revealed in [4]. In [5, 6], the spectrum attributed to the paramagnetic Gd subsystem was
also observed.

The reason for the emergence of this magnetic structure of GdMn$_2$O$_5$ should be sought for in
properties of the ground state $^6S_{7/2}$ of the Gd$^{3+}$ ions with a large spin S=7/2 which weakly interact with
the lattice. The magnetic state of the Gd subsystem is mainly determined by the Gd – Mn exchange
interaction. This differs GdMn$_2$O$_5$ from other RMn$_2$O$_5$ with R ions characterized by strong spin-orbital
interactions in which complex magnetic structures are typically formed [2]. The state of the R subsystem in these R Mn$_2$O$_5$ is mainly determined by the crystal field and, to a lesser extent, the R-Mn exchange.

3. Polarization of GdMn$_2$O$_5$

To explain the magnetic origin of ferroelectricity in RMn$_2$O$_5$, the model of exchange striction caused by the characteristic charge and spin orderings of Mn$^{3+}$ and Mn$^{4+}$ ions along the b axis is typically used. These orderings result from a paired arrangement of the Mn$^{3+}$-Mn$^{4+}$ ions along the b axis. The mutual orientation of the spins of these ion pairs alternates, i.e., ferromagnetic pairs alternate with antiferromagnetic ones. A strong double exchange arises between the ferromagnetic spins of Mn$^{3+}$-Mn$^{4+}$ ion pairs. A weaker indirect exchange is characteristic of the antiferromagnetic spins of such pairs. As a result of the exchange striction, distances between ferromagnetic and antiferromagnetic pairs change. This breaks the lattice centrosymmetricity and gives rise to the polarization along the b axis [3]. This mechanism can explain only a small contribution of the Mn-subsystem into the polarization (typically of the order of 0.01 – 0.05 μC/cm$^2$) usually observed in RMn$_2$O$_5$ [2]. As noted above, an order of magnitude stronger polarization induced by a symmetric Gd-Mn exchange is observed in GdMn$_2$O$_5$. Since the Gd spin configuration is similar to the manganese one, the difference in the Gd-Mn exchange interactions for the Gd- Mn$^{3+}$ and Gd- Mn$^{4+}$ ion pairs along the b axis leads to additional exchange striction, non-centrosymmetricity, and growth in the total polarization.

The polarization in single crystals of GdMn$_2$O$_5$ along the b and c axes was studied by measuring the pyrocurrent after application of a polarizing electric field and without it (at E = 0). Polarization was calculated by integrating the pyrocurrent measured during sample heating with a constant temperature variation rate.

![Figure 2. Polarizations (left axis) and dielectric permittivities (right axis) in some electric fields, at set of frequencies. E||b.](image1)

![Figure 3. Pyrocurrent in some electric fields. E||b.](image2)

An abnormally high polarization in GdMn$_2$O$_5$ along the b axis was confirmed (Fig. 2). Along with this, it was found that the maxima in pyrocurrent near 30 K in the case of E = 0 and after application of a polarizing electric field E = ± 2.7 kV/cm (Fig. 3) were similar. This means that rigid polarization is formed in the high internal field and the usual 180-degree domain structure is not formed in GdMn$_2$O$_5$. Probably, only sufficiently large rigid bulk domains with different polarization orientations along the b axis that arise due to elastic strains and defects in real crystals can exist in GdMn$_2$O$_5$. Such a picture is characteristic of antiferromagnetic domains, for example, in Cr$_2$O$_3$ [11].

4. Low-frequency (30 – 50 GHz) magnetic dynamics

Let us consider the low-frequency magnetic dynamics of GdMn$_2$O$_5$. Studies of the dynamics of a set of RMn$_2$O$_5$ crystals with different R ions revealed similar sets of FMRs for these crystals [7, 8]. We attributed these resonances to responses of individual superlattice layers formed due to phase separation and charge carrier selforganization in the crystal bulk. Superlattices occupied a small
volume of the initial crystal and at $T < 30-40$ K did not interact with each other. Superlattice layers were ferromagnetic and contained different amounts of manganese ions with different valences and charge carriers. An additional small polarization was formed in the superlattice layers along the crystal c axis. We supposed that superlattices were domain walls between bulk domains [8, 9].

Since manganese ions with different valences are located in the layers perpendicular to the c axis at distance $\frac{1}{4}c$, there is a finite probability of tunneling of the $e_g$ electron from the Mn$^{3+}$ ion to the Mn$^{4+}$ ion lying in the neighboring layers along the c axis (double exchange). In this situation ferromagnetic Mn$^{3+}$-Mn$^{4+}$ ion pairs and electrons that recharge these pairs emerge in all the layers containing Mn ions. Because of an energetically favorable phase separation typical of all the manganites containing Mn$^{3+}$ and Mn$^{4+}$ ions [12, 13], these ferromagnetic pairs and electrons are accumulated in isolated regions inside the antiferromagnetic dielectric matrix. The double exchange and the Jahn-Teller effect (for the Mn$^{3+}$ ions in octahedra) leads to attraction of charge carriers and ferromagnetic pairs, while the Coulomb repulsion forms dynamically equilibrated isolated superlattices (selforganization process).

Fig. 4 shows a set of FMR lines pointing to formation of superlattices in GdMn$_2$O$_5$. We suppose that the Gd and Mn ions that are present in the crystal regions occupied by the superlattices form a subsystem of paramagnetic Gd ions magnetized by ferromagnetic Mn ions. This system is responsible for the additional paramagnetic branch of the spectrum of the Gd subsystem reported in [6] and a difference between the RMS and NRMS spectra observed in [4].

Fig. 5 presents a small polarization along the c axis induced by the superlattices. Like in the case of a giant polarization along the b axis of the basic crystal bulk, the polarization of the superlattices is induced by the internal field. Small anomalies in the pyrocurrent and polarization near $T_{N2}$ are seen. In addition, there are pyrocurrent peaks near 130 K. We attribute the peaks to the disappearance of the polar order in the superlattices at this temperature.

To summarize, the presence of an abnormally high polarization along the b axis in GdMn$_2$O$_5$ as compared with other RMn$_2$O$_5$ has been confirmed. It has been found that this unidirectional rigid polarization is induced by the internal field. Like in all multiferroics with manganese ions of variable valences, uniaxial superlattices (normal to the c axis) are formed in GdMn$_2$O$_5$ due to phase separation and charge carrier selforganization. We suppose that the superlattices are domain walls between rigid bulk domains. A weak polarization along the c axis is formed inside the superlattice layers. The interrelated Gd – Mn antiferromagnetic order forming the basic rigid domains with a giant polarization along the b axis gives rise to the AFMR branch [6]. The superlattices are responsible for the paramagnetic branch of excitations [6] and a difference in the NRMS and RMS spectra [4].
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