PROCEEDINGS

2020 7th International Congress on Energy Fluxes and Radiation Effects (EFRE)

Tomsk, Russia, September 14 – 26, 2020

SPONSORED BY

IEEE Nuclear and Plasma Sciences Society

Institute of High Current Electronics of the Siberian Branch of the Russian Academy of Sciences

National Research Tomsk Polytechnic University

Tomsk Scientific Center of the Siberian Branch of the Russian Academy of Sciences

Chairman

Nikolay Ratakhin
Institute of High Current Electronics, Tomsk, Russia

Co-Chairman

Andrey Yakovlev
National Research Tomsk Polytechnic University, Tomsk, Russia

Alexey Markov
Tomsk Scientific Center SB RAS, Tomsk, Russia

Program Chairman

Alexander Batrakov
Institute of High Current Electronics, Tomsk, Russia

Program Co-Chairman

Edl Schamiloglu
University of New Mexico, Albuquerque, USA

7th International Congress on Energy Fluxes and Radiation Effects (EFRE) - 4th International Conference on New Materials and High Technologies -
Tomsk - 2020

Features of the Permeability Spectra of CoZnW Hexaferrites in the Spin-Reorientation Phase Transition Region

Victor Zhuravlev
National Research
Tomsk State University
36 Lenin Ave., 634050,
Tomsk, Russia
ptica@mail.tsu.ru

Valentin Suslyaev
National Research
Tomsk State University
36 Lenin Ave., 634050,
Tomsk, Russia
susl@mail.tsu.ru

Alexandra Pavlova
National Research
Tomsk State University
36 Lenin Ave., 634050,
Tomsk, Russia
apr@mail.tsu.ru

***Abstract*—The hexaferrites of the $Co_{2-x}Zn_xW$ system have a number of outstanding properties among other hexaferrites. This makes them promising both for obtaining new physical data and for practical use. In this paper, we analyze the concentration and temperature dependences of the resonance frequencies of natural ferromagnetic resonance and the damping constant in the equation of motion of the magnetization vector of these materials in the vicinity of spin-reorientation phase transitions. It is shown that these hexaferrites can find practical application in the entire microwave frequency range.**

Keywords—hexaferrites, magnetic permeability spectra, magnetocrystilline anisotropy, spin-reorientation phase transitions.

I. INTRODUCTION

Ferrites with hexagonal crystal structure (called hexaferrites hereinafter) composition $BaMe_2Fe_{16}O_{27}$ (Me_2W) have maximum values of the saturation magnetization among the hexaferrites and their Curie temperature is high enough [1]. Therefore, they are promising materials for various practical applications. Here, the letter Me denotes a bivalent metal ion Me^{2+}.

An important characteristic of the hexaferrites is the magnitude and sign of the magnetocrystilline anisotropy (MCA) field. The values of MCA fields of the Me_2W hexaferrites are within the limits of 10–20 kOe for bivalent Fe^{2+}, Ni^{2+}, Mg^{2+} , Zn^{2+} and Cu^{2+} ions and their combinations [1]. These materials possess MCA of the easy magnetization axis (EMA) type at such substitutions. This axis is the hexagonal axis *c* of the crystal lattice. The high value of saturation magnetization of W-type hexaferrites provides a large magnitude of the permeability and hence they are promising for use in various microwave devices. However, the application of hexaferrites of this structural type as a radar absorbing materials is limited by millimeter wavelengths with frequencies of ~ 30–60 GHz because of their strong anisotropy fields.

The use of Co^{2+} ion as Me^{2+} leads to the fact that the magnetocrystilline anisotropy of the hexaferrite changes radically from those of the ions listed above. The Co_2W hexaferrite has anisotropy of the easy magnetization plane (EMP) type. The anisotropy field relative to the hexagonal axis is more than -20 kOe at room temperature [1, 2]. The minus sign hereinafter means the EMP-type anisotropy. The spin-reorientation phase transition (SRPT) from EMA to EMP type anisotropy will be observed in solid solutions of the Co^{2+} containing hexaferrites combined with any of the above-listed ions with increasing cobalt ion content. SRPT transitions are observed not only for concentration but also for temperature changes [2–4]. Neutron-diffraction investigations of $Co_{2-x}Zn_xW$ system hexaferrites were carried out in [3]. They have demonstrated that the EMA↔EMP temperature SRPT proceeds through the easy magnetization cone (EMC) phase. The values of the MCA fields can change in a wide range with changes of the Co^{2+} ion concentration. It offers the possibilities of W-type hexaferrite application for radar absorbing materials in the entire microwave range starting from ~ 1 GHz [4, 5].

II. THEORETICAL BACKGROUNDS

The foundations of the theory of permeability spectra of polycrystalline hexaferrites in the natural ferromagnetic resonance (NFMR) region were developed by us in [5, 7, 8]. The calculations were carried out in the approximation of independent grains. This approximation is well satisfied for hexaferrites with the large values of magnetocrystalline anisotropy fields. The calculation for single-domain particles of ellipsoidal shape was performed in [7]. The effect of the domain structure on NFMR was studied in [5, 8]. It was shown that two absorption maxima can be observed in the spectra of $\mu''(f)$ depending on the shape of the sample, the type of domain structure, magnitude and sign of the MCA fields.

According to [1, 5, 8], the main contribution to the PS of the hexaferrites comes from the rotation of the magnetization vector in the microwave frequency range. The dispersion of the permeability spectra observed in the microwave range is related to NFMR. Consequently, the concentration and temperature dependences of the PS of the $Co_{2-x}Zn_xW$ system hexaferrites in the vicinity of the SRPT should have features. In further analysis of the permeability spectra, we restrict ourselves to calculations for single-domain noninteracting spherical particles.

The work was supported by Tomsk State University Improvement Program and supported by the RFBR grant No. 19-32-90226 “Postgraduate students”.

978-1-7281-2686-9/20/$31.00 ©2020 IEEE

Most of the articles devoted to the use of the $Co_{2-x}Zn_xW$ hexaferrite system in the microwave frequency range do not consider the effect of the SRPT concentration and the temperature on the permeability spectra ($\mu^*(f) = \mu'(f) - i\mu''(f)$) [6]. Here $\mu'(f)$ is the real and $\mu''(f)$ is the imaginary parts of the permeability. The aim of this work is to study the features of some main parameters of the permeability spectra (PS) of the hexaferrites $Co_{2-x}Zn_xW$ system with a change in the concentration of zinc ions and temperature.

In this case, in the region of existence EMP type anisotropy, the resonance frequency (f_r) of the NFMR is determined by the formula:

$$2\pi f_r = \gamma(|H_\Theta|H_\Phi)^{1/2}, \tag{1}$$

and in the EMA region:

$$2\pi f_r = \gamma H_{a1}. \tag{2}$$

Here, $H_\Theta = H_{a1} + H_{a2} + H_{a3}$ is the anisotropy field relative to the basal plane, H_{a1} is the anisotropy field along the hexagonal axis and $H_{ai} = 2ik_i/M_S$. $H_\Phi = 36\ \kappa_4/M_S$ is the anisotropy field in the basal plane, k_i are the i-th order anisotropy constants. M_S is the saturation magnetization, γ is the magnetomechanical ratio.

The magnitude of the imaginary part of the permeability of the isotropic polycrystalline sample at resonance in both cases can be estimated as

$$\mu''_r = (\gamma 4\pi M_S)/(3*2\pi f_r\alpha), \tag{3}$$

where α is the dissipation parameter in the equation of motion of the magnetization vector. Formulas (1) - (3) were obtained under the assumption that dissipation is small. The H_{a1} MCA field changes sign at the SRPT transition EMA ↔ EMP. Therefore a minimum should be observed in the temperature or the concentration dependences of $2\pi f_r$ according to (1), (2). In addition, an increase in the dissipation parameter can be expected in the SRPT region.

III. SAMPLE PREPARATION AND MEASUREMENT PROCEDURES

An experimental study was carried out on polycrystalline samples of the $Co_{2-x}Zn_xW$ system ($0.5 \le x \le 1.5$). Samples were synthesized using standard two-stage ceramic technology. Precursors were AR grade oxides and salts. The phase composition and lattice parameters of the samples were examined by X-ray diffraction method (SHIMADZU XRD-6000 polycrystalline diffractometer in Bragg-Brentano geometry). The PDF4+ computer database of X-ray powder diffractometry data of the International Centre for Diffraction Data (ICDD, Denver, United States) was used for the qualitative analysis of phase composition. Quantitative analysis of the phase composition was carried out using the Powder Cell 2.4 computer software. The content of the target W phase in the materials was not less than 80%, the density of the samples was not less than 0.8 from the X-ray density.

The introduction of Zn^{2+} ions results in an appreciable increase in the saturation magnetization in this hexaferrites system. The extreme compositions of the system possess magnetocrystilline anisotropies of various type. At $x < 1.3$, an EMP state is observed and at $x > 1.3$, an EMA state is observed.

The region of the complex behavior of the PS of hexaferrites occupies a wide frequency band. Therefore, it is impossible to be limited to one method of the measurement. At low frequencies (0.1–1 GHz), we used the coaxial-waveguide method with toroidal samples. In a high-frequency range (1–27 GHz) we applied a rectangular transmission-type cavity with an oscillation mode H_{10p}. The samples were taken in the form of rods overlapping the cross section of the waveguide. The wide band of resonance measurements is obtained using a set of resonators and the method of frequency variation. On the boundary of this method (0.2–1.5 GHz), the measurements were carried out using an irregular microstrip resonator [9] made of a high-permittivity ceramics, with a sample in the form of a thin plate with a size corresponding to the air gap between the strip lines. Some discrepancy in the results of measurements was observed on the boundaries of methods. It could be caused by the use of various approaches for the different methods of measurements. The Kramers-Kronig relations were used to match and smooth the results by the method proposed in [10].

IV. CONCENTRATION DEPENDENCES OF THE PARAMETERS OF THE PERMEABILITY SPECTRA AT ROOM TEMPERATURE

Fig. 1 shows the concentration dependences of the resonance frequency of the NFMR determined from the maximum of $\mu''(f_r)$ (curve 1) and the dissipation parameter $\alpha(x)$ (curve 2) calculated by (3) from the value of the imaginary part of the permeability μ''_r at resonance. The measurements were carried out at room temperature (20□). The concentration dependence of $f_r(x)$ is normalized to the value of $f_r(x=1) = 6.1$ GHz.

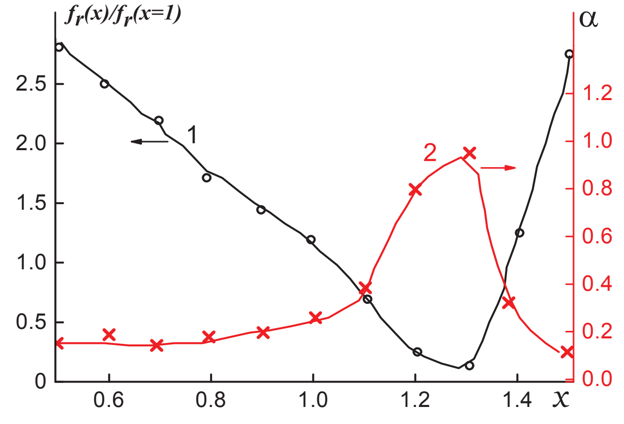

Fig. 1. Concentration dependence of $f_r(x)/f_r(x = 1.0)$ determined from the maximum of $\mu''(f_r)$ (curve 1) and the concentration dependence of the dissipation parameter $\alpha(x)$ (curve2). The measurements were carried out at room temperature.

The frequency $f_\mathrm{r}(x)$ decreases with increasing x, reaches a minimum near the concentration of ions Zn^{2+} $x \approx 1.3$ and then quickly increases. The minimum value of $f_\mathrm{r}(x{=}1.3)$ is 0.6 GHz. The maximum is observed in the concentration dependence of $\alpha(x)$ at $x \approx 1.3$. Neutron diffraction studies of the hexaferrites $Co_{2\text{-}x}Zn_xW$ system [3] showed that up to concentrations $x \leq 1.2$ there was the EMP state at room temperature. The EMC state is observed for ferrite with $x_c = 1.3$. Materials with $x \geq 1.38$ have EMA states. Thus, anomalies observed in the dependences $f_\mathrm{r}(x)/f_\mathrm{r}(x{=}1.0)$ and $\alpha(x)$ are related to SRPT. According to Fig. 1, the change in the concentration of zinc ions allows the frequency of NFMR to widely vary.

V. TEMPERATURE DEPENDENCES OF THE PARAMETERS OF THE PERMEABILITY SPECTRA

More detailed information on the behavior of the permeability spectra in the region SRPT EMA ↔ EMP can be obtained from the study of their temperature dependences. Fig. 2 shows the normalized temperature dependences $f_\mathrm{r}(T)/f_\mathrm{r}(T{=}20\square)$ (curve 1) and the temperature dependence of the damping constant $\alpha(T)$ (curve 2) of $Co_{2\text{-}x}Zn_xW$ hexaferrite with the zinc ion concentration $x = 1.0$. The resonant frequency passes through a minimum near $T_2 = 80\square$ with increasing temperature. The temperature dependence has one more minimum at $T_1 = 130°C$. The dependence $\alpha(T)$ at these temperatures also has features. Curve 3 in Fig. 2 represents the temperature dependence of the angle of direction of easy magnetization ($\theta(T)$) of a given hexaferrite. It is calculated from the neutron diffraction data.

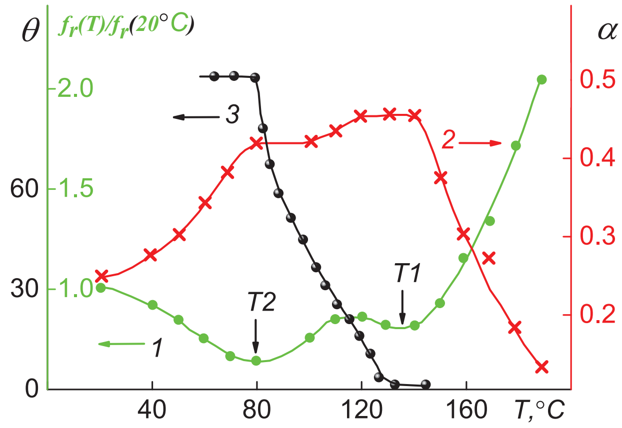

Fig. 2. Temperature dependences of the normalized resonance frequency NFMR $f_\mathrm{r}(T)/f_\mathrm{r}(20\square)$ (curve 1) and $\alpha(T)$ (curve 2) of the hexaferrite $Co_{2\text{-}x}Zn_xW$ (x=1). Curve 3 is the calculated from the neutron diffraction data temperature dependence of the angle of easy magnetization direction $\theta(T)$ of the given hexaferrite.

It can be seen that the temperatures at which $f_\mathrm{r}(T)$ passes through the minimum correlate well with the SRPT EMP↔EMC (T_2) and EMC↔EMA (T_1) temperatures. The damping constant α is maximum in the interval of the conical phase and rapidly decreases outside the SRPT region.

The anomalies observed in the temperature dependence of the NFMR frequency can be explained as follows. EMP state is implemented with an increase in the temperature up to $T \leq T_2$. In this region the MCA fields are related by the following inequalities: $H_{a1} < 0$, $|H_{a1}| > H_{a2} + H_{a3}$. In this case $H_\Theta < 0$ and the resonance frequency is determined by (1). The MCA field H_Θ changes sign at $T = T_2$. In the temperature range $T_2 \leq T \leq T_1$ the magnitude of the MCA field is $|H_{a1}| \leq H_{a2} + H_{a3}$. Therefore, the conical configuration is energetically more favorable. A further increase in the temperature leads to the fact that at $T = T_1$ MCA field H_{a1} changes sign. Therefore, in the temperature range $T > T_1$ the EMA state is observed. The resonance frequency of the NFMR in this case is determined by (2).

VI. CONCLUSION

Thus, the behavior of the permeability spectra of the hexaferrites $Co_{2\text{-}x}Zn_xW$ system depending on the concentration of Zn^{2+} ions and temperature is explained by the NFMR theory. In this theory, it is considered that the main role in the processes of magnetization at microwave frequencies is played by the processes of rotation of the magnetization vector in the internal MCA fields. An investigation of the permeability spectra allows additional information to be obtained not only about the behavior of the spin system in the vicinity of SRPT but also about the values and signs of the MCA constants of polycrystalline hexaferrites.

A change in the concentration of Zn^{2+} ions makes it possible to vary the resonance frequency of the NFMR of $Co_{2\text{-}x}Zn_xW$ hexaferrites in a wide range (by tens of times). This allows these materials to be used in devices operating in different microwave frequency ranges.

ACKNOWLEDGMENT

The work was supported by Tomsk State University Improvement Program and supported by the RFBR grant No. 19-32-90226 “Postgraduate students”.

Experimental studies in this work were carried out on the equipment of the collective use center of Tomsk State University «Center for Radiophysical Measurements, Diagnostics and Research of Parameters of Natural and Artificial Materials».

REFERENCES

[1] J. Smit and H. P. J. Wijn, *Ferrites*. London: Cleaver-Hume Press Ltd., 1959.

[2] A. Paoluzi, F. Licci, O. Moze and G. Turilli, “Magnetic, Mossbauer, and neutron diffraction investigations of W-type hexaferrite BaZn2–xCoxFe16O27 single crystals,” *J. Appl. Phys*., vol. 63, pp. 5074–5080, May 1988.

[3] E. P. Naiden, V. I. Maltsev, G. I. Ryabtsev, “Magnetic Structure and Spin-Orientational Transitions of Hexaferrites of the BaCo2-xZn$_x$Fe$_{16}$O$_{27}$ System,” *Phys. Ptatus Solidi A*, vol. 120, no. 1, pp. 209–220, February 2006.

[4] Z. W. Li, Chen Linfeng and C. K. Ong, “High-frequency magnetic properties of W-type barium-ferrite BaZn2–xCo$_x$Fe$_{16}$O$_{27}$ composites,” J. Appl. Phys., vol. 94, pp. 5918–5924, November. 2003.

[5] V. A. Zhuravlev and V. I. Suslyaev, “Analysis of the microwave magnetic permeability spectra of ferrites with hexagonal structure,” *Russian Physics Journal*, vol. 49, pp. 1032–1037, September 2006.

[6] R. C. Pullar, “Hexagonal ferrites: A review of the synthesis, properties and applications of hexaferrite ceramics,” *Prog. Mat. Sci.*, vol. 57, pp. 1191–1334, September 2012.

[7] V. A. Zhuravlev, “Magnetic permeability spectrum of ferroxplans in the NFMR region. Like noninteracting particles,” *Soviet Physics Journal*, vol. 32, pp. 33–36, January1989.

[8] V. A. Zhuravlev, “Magnetic Permeability Spectra of Hexaferrites in the Microwave Range,” *The Physics of Metals and Metallography*, vol. 100, Suppl. 1, pp. S79–S71, October 2005.

[9] V. I. Suslyaev, V. A. Zhuravlev, T. D. Kochetkova and S. V. Sudakov, “An Automated Setup for Investigating the Temperature Dependence of the Permittivity Spectra of Polar Liquids in the Range of 0.1–1.25 GHz,” *Instruments and Experimental Techniques*, vol.46, pp. 672–676, May 2003.

[10] V. A. Zhuravlev and V. I. Suslyaev, “Analysis and correction of the magnetic permeability spectra of Ba3Co2Fe24O41 hexaferrite by using Cramers–Kronig relations,” *Russian Physics Journal*, vol. 49, pp. 840–846, August 2006.