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Nonlinear magnetoelectric effects in flexible composite ferromagnetic – Piezopolymer structures

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ABSTRACT

Nonlinear magnetoelectric (ME) effects in a flexible composite planar structure, containing mechanically coupled layers of amorphous FeBSiC ferromagnet and PVDF piezoelectric polymer have been experimentally investigated. Under the action of a weak harmonic magnetic field h with frequency $f = 50–1000$ Hz and tangential bias magnetic field $H = 1–80$ Oe, the structure generated a voltage of the same frequency. The efficiency of linear ME conversion reached 3.4 V/(cm·Oe) for the optimum bias field $H_m \approx 15$ Oe. On increasing the excitation field up to $h \sim 7$ Oe, the structure generated second and third harmonics with efficiencies of $\sim$25 mV/(cm·Oe^2) and $\sim$2.5 mV/(cm·Oe^3), respectively. The amplitudes of the harmonics were not monotonous functions on the bias field H and grew with the increase in the alternating field h. Under the action of two alternating fields with different frequencies f_1 and f_2, the structure generated ac voltages with frequencies equal to the sum and difference frequencies $f_1 \pm f_2$. The efficiency of magnetic fields mixing reached a maximum of $\sim$30 mV/(cm·Oe^2) in the absence of the bias field. The effects of harmonics generation and magnetic fields mixing arise due to the nonlinear dependence of the ferromagnet's magnetostriction λ on the bias field H. The efficiency of the nonlinear processes is proportional to the derivatives of the magnetostriction over magnetic field. The nonlinear ME effects in the ferromagnet-piezopolymer flexible structures can be used to design high-sensitivity dual ac/dc magnetic field sensors and energy harvesting devices.

1. Introduction

Magnetoelectric (ME) effect in composite materials exhibits itself as an electrical polarization of a sample in an external magnetic field (direct effect) or a change of magnetization of the sample in an external electric field (converse effect) [1]. The effect is observed in single-phase materials and in composite materials which simultaneously posses magnetic and electric ordering [2]. The largest direct ME effect was observed in planar structures containing alternating ferromagnetic (FM) and piezoelectric (PE) layers. The ME effect in such structures arises due to a combination of magnetostriction of the FM layer and piezoelectricity of the PE layer through mechanical coupling between the layers [3]. The magnitude of the direct effect is characterized by the ME voltage coefficient $\alpha_E = \delta E/\delta H$, where δE is the amplitude of the electric field generated by the magnetic field δH.

It was shown [2,4], that in structures containing FM layers with high magnetostriction λ (metals Ni, Co, alloys FeCo, FeGa, Terfenol-D, amorphous alloys, ferrites) and PE layers with large piezomodulus d (ceramic lead zirconate titanate (PZT), lead magnesium niobate - lead titanate crystals, AlN, langatate, quartz) the ME coefficient can reach values of $\alpha_E \sim 1–10$ V/(cm.Oe). The effect can be enhanced by up to two orders of magnitude when the excitation field frequency coincides with the frequency of acoustic resonance of the structure [5], which is defined by the size and stiffness of the material used. These resonance frequencies for bulk samples are typically in the range from a few kHz to hundreds of kHz. Promising applications of the ME effect in composite structures are: highly sensitive magnetic field sensors, wireless energy harvesting devices, new data recording and storage elements, and electrically tuned radio-frequency signal processing devices [4,6–8].

In recent years, the interest in the study of ME effects in composite structures comprising piezopolymers, especially polyvinilidene fluoride (PVDF), has increased significantly [9–11] because of a number of advantages that PVDF has over ceramic and single crystal piezoelectric materials [11,12]. In particular, the PVDF fabrication technology is well developed and, unlike the ceramic piezoelectrics, it does not require high temperature processing.

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Although the PVDF piezomodulus is not very large, $d_{31} \approx 6–20$ pC/N, this is compensated by its low permittivity $\varepsilon \approx 12$, resulting in a ratio $d_{31}/\varepsilon \sim 1$, which is several times higher than that of most crystals and piezoceramics. The polymer has a high resistivity ($\rho > 10^{14}$ Om·cm) and small dielectric losses (tg$\delta \approx 0.02$). The combination of all these properties imply the expectation of high values of the ME coefficient for the structures consisting of PVDF layers. In addition, the Young's modulus of the PVDF, $Y \approx 3$ GPa, is an order of magnitude smaller than that of the single crystals and piezoelectric ceramics, i.e. it is usually referred to as "soft" material. This makes PVDF ideal for the use in the low frequency range $\sim 1–10^3$ Hz applications, which coincide with the frequencies of natural and industrial vibrations as well as magnetic field frequencies. Moreover, the PVDF can be used to fabricate flexible structures that can be deposited onto surfaces of complex forms, it has a significantly lower cost in comparison with crystalline and ceramic piezoelectrics and is biocompatible in some cases, which is important for medical applications.

The ME effect was first observed in the planar structure of Terfenol-D-PVDF [9], in structures with PVDF layers of the following compositions: PZT/Terfenol-D/PVDF [13], Ni-Mn-Ga-PVDF [14], PVDF-Vitrovac [15–17], and in structures with nanometer-thick layers of Fe-PVDF-Fe [18]. Flexible structures exhibiting ME effects were first made by bonding PVDF and amorphous Metglas layers [19], resulting in non resonance ME coefficients of $\alpha_E = 7.2$ V/(cm·Oe) and $\alpha_E \approx 238$ V/(cm·Oe) at the resonance frequency of 50 kHz. In subsequent works [20–23] it was shown that Metglas is the most suitable material for fabrication of flexible ME structures with PVDF layers, because it has high magnetostriction coefficient $\lambda \sim 20–30$ ppm, it saturates in low magnetic fields $H_S \sim 50$ Oe, and PVDF layers can be deposited directly on the ferromagnetic layer [24] without using glue. This allowed to achieve, under resonance conditions, the maximum ME coefficient of $\alpha_E = 850$ V/(cm·Oe) in structures containing PVDF layers. Based on such structures, magnetic field sensors with limit of detection as small as $\sim$1 pT [25], current sensors [26], and the energy harvesters [27] have been demonstrated.

It should be noted that till now the ME effects in structures with piezopolymer layers were investigated only for small amplitudes of excitation magnetic fields and the signal generated by the structure was registered at the frequency of excitation magnetic field. From physical point of view and for various applications the study of nonlinear ME effects in the polymer-based structures is of great interest. Such effects may be observed at relatively large amplitudes of the fields due to nonlinear dependence of the magnetostriction of a ferromagnetic layer on the magnetic field [28–32].

In the present paper we report, for the first time, experimental studies of the nonlinear ME effects in composite layered FM-PE structures, consisting of piezoelectric polymer PVDF and amorphous alloy Metglas. We show that, for two ac magnetic field excitations applied simultaneously, the PVDF layer effectively generates a voltage of multiple frequencies with values equal to the difference and sum of the excitation frequencies, especially when the amplitudes of alternating magnetic fields acting on the structure are comparable or larger than the dc bias field. The first part of the paper describes the structure under investigation and the experimental setup, followed by the results of experimental investigation of linear and nonlinear ME effects in the Metglas-PVDF structure, discussion of the results, and conclusions.

2. Samples and experimental setup

Fig. 1a shows a schematic view of the structure under investigation, while Fig. 1b shows its appearance. The ferromagnetic layer was made of amorphous iron-based ribbon FeBSiC (Metglas Inc.). It has lateral dimensions of 10 mm × 14 mm and thickness of 27 μm. The choice of Metglas is due to its high saturation magnetostriction $\lambda_s \approx 20 \cdot 10^{-6}$, sufficiently small saturation field $H_S \sim 50$ Oe, and good mechanical properties, including high flexibility. The piezoelectric layer was made of commercially available PVDF film (TE Connectivity Ltd.). It had lateral dimensions of 10 mm x 14 mm and the thickness of $b = 28$ μm. The PVDF layer surfaces were covered with 3 μm thick Ag electrodes. The PVDF layer had capacitance $C = 0.55$ nF measured at 1 kHz frequency, which corresponds to the dielectric permittivity $\varepsilon = 11.6$. The piezoelectric modulus of the PVDF was $d_{31} \approx 10$ pC/N. The Metglas and PVDF layers were mechanically coupled under the press using the fast dry "Loctite" adhesive.

The block-diagram of the experimental setup is shown in Fig. 2. The structure was placed in a uniform bias dc magnetic field $H = 0–100$ Oe created by a pair of Helmholtz coils, which were fed by dc current from the "DC power supply" AKIP 1125. Alternating magnetic fields $h_1 \cos(2\pi f_1 t)$ and $h_2 \cos(2\pi f_2 t)$ with amplitudes h_1, h_2 up to 7 Oe and frequencies in the range $f_1, f_2 = 10–5$ kHz were created by two coaxial electromagnetic coils K_1 and K_2, which were powered by two independent generators "AC Gen1" and "AC Gen2", both Agilent 33210A. Magnetic fields were measured using "Gaussmeter" LakeShore 421 with accuracy of 0.1 Oe. The ME signal was amplified using an "Amp" SR 560 amplifier and registered using an "Oscilloscope" TDS 3032A. The amplitude of generated ac voltage was measured using the "Voltmeter" AKIP-2401. The frequency spectra of the output signal were registered by the "Network Analyzer" SR770. The entire experiment and data processing were fully automated and controlled using a special LabView program.

3. Experimental results

At the first stage, we have measured the frequency and field characteristics of the direct ME effect in the described structure under its excitation in linear regime with a small amplitude ac magnetic field. Fig. 3a shows frequency dependence of the voltage $u(f)$ generated by the PVDF layer under excitation with magnetic field amplitude $h = 1$ Oe and bias field $H = 15$ Oe. The structure generates voltage in the frequency range from $\sim$50 Hz up to $\sim$5 kHz. At low frequencies $f < 100$ Hz the voltage decreases due to finite conductivity of the PE layer [33], and at higher frequencies $f > 2$ kHz the voltage decreases due to lowering in the amplitude of excitation magnetic field caused by the inductance of the coils. The low-Q peak near the frequency $\sim$1.2 kHz with the quality factor $Q \approx 5$ occurs, as it was shown by the formulas assessment [34], due to the resonance excitation of bending oscillations of the structure. The maximum value of the ME coefficient at resonance frequency reached $\alpha_E \approx 3.4$ V/(cm·Oe). At low frequencies $\sim$200 Hz–1 kHz below the resonance the ME coefficient was $\alpha_E \approx 0.3–1.2$ V/(cm·Oe).

Fig. 3b shows the magnetic field dependence of the generated voltage $u(H)$ when the structure was excited by ac field $h = 1$ Oe with a frequency $f = 500$ Hz. The response is typically characteristic for planar structures [2]: the voltage first grows almost linearly with increasing of H, reaches a maximum at $H_m \approx 15$ Oe, which corresponds to the maximum of piezomagnetic coefficient $\lambda^{(1)}(H) = \partial\lambda/\partial H$ of the ferromagnetic layer, and then gradually decreases with increasing H during the saturation of the magnetostriction. From data presented in Fig. 3, the ME coefficient was estimated as $\alpha_E = u/(bh) \approx 0.47$ V/(cm·Oe) at optimum bias field H_m.

At the second stage the characteristics of ME effect in the Metglas-PVDF structure have been measured in the spectral region under single-frequency excitation for various values of ac and dc