Journal of Applied Physics

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Cite as: J. Appl. Phys. **124**, 134101 (2018); https://doi.org/10.1063/1.5044598
Submitted: 14 June 2018 . Accepted: 10 September 2018 . Published Online: 04 October 2018

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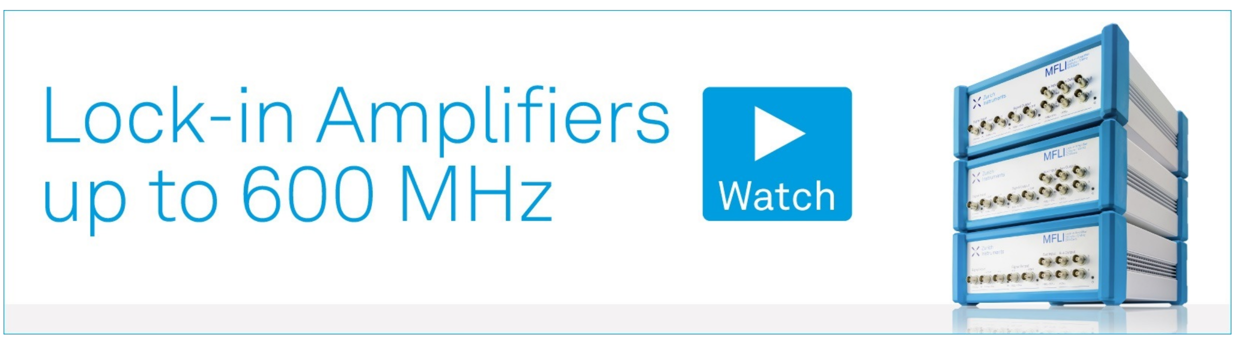

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JOURNAL OF APPLIED PHYSICS **124**, 134101 (2018)

The magnetoelectric ME_E-effect in the $SmFe_3(BO_3)_4$ multiferroic in dc and ac electric fields

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(Received 14 June 2018; accepted 10 September 2018; published online 4 October 2018)

The inverse magnetoelectric ME_E-effect in the $SmFe_3(BO_3)_4$ single-crystal sample in an applied electric field has been studied. The electric field E consists of two components: a constant one, e_0, and a variable one, $e \times \cos(\omega t)$. The investigated compound evokes great interest due to the existence of both linear and quadratic contributions to the magnetoelectric effect. According to theoretical analysis, the effective susceptibility of the first harmonic of magnetic moment oscillations depends on the dc electric field component e_0. Indeed, according to the measurement data, the dc field e_0 significantly affects the ME_E-effect first-harmonic amplitude: depending on the e_0 sign, these oscillations can be either amplified or suppressed. This offers an opportunity for controlling the magnetic moment oscillation amplitude at the applied electric field frequency, including the signal modulation, which is promising for application. In the applied dc field e_0, a slight change in the susceptibility of the ME_E-effect term quadratic to the electric field was detected. The mathematical apparatus used correctly describes the qualitative dependence of the ME_E-effect amplitude on the dc field e_0, while the quantity appears to be approximately twofold overestimated. *Published by AIP Publishing.* https://doi.org/10.1063/1.5044598

I. INTRODUCTION

Multiferroics capture much attention of researchers due to their high potential for use in designing electronic devices, including current and magnetic-field sensors, logical elements, and novel random access memory, optoelectronic, and spintronic devices.[1–4] A magnetoelectric material can exhibit the magnetoelectric effect of two types: the direct ME_H-effect, that is, the sample's electric polarization variation in an external magnetic field [$\Delta P(H)$]; and the inverse ME_E-effect, that is, the sample's magnetic moment variation in an external electric field [$\Delta M(E)$]. The overwhelming majority of scientific works have been devoted to the ME_H-effect, while there has been a lack of literature data on the ME_E-effect. This is due to the difficulties related to the development of experimental setups for measuring the ME_E-effect. It is noteworthy that the ME_E-effect was detected first in 1960 by Astrov.[5]

In his work, Astrov investigated the magnetization induced by an electric field. A sample of the Cr_2O_3 single crystal was located between the electrodes, to which an alternating voltage was applied at a frequency of 10 kHz. The sample was located in a pick-up coil, the signal from which was fed to the input of the amplifier. Due to the magnetoelectric effect, when the external alternating electric field was applied, the magnetic moment of the sample changed, and a signal proportional to the amplitude of the oscillation of the magnetic moment was induced in the pick-up coil. Later, the measurements were repeated by other researchers using oriented samples of Cr_2O_3.[6]

In more recent works,[7,8] measurements of the reverse magnetoelectric effect at experimental installations based on superconducting quantum interference device (SQUID) magnetometers were made. An interesting method for measuring the magnetoelectric effect is given in Ref. 9, where measurements of magnetic permeability were made as a function of frequency and a constant electric field using wave measurement methods.

The direct magnetoelectric ME_H-effect was first measured by the quasistatic method of Folen and Rado in 1961 on a Cr_2O_3 single crystal.[10] Silver paste was used to prepare electrical contacts on the sides of the sample for magnetoelectric measurements. These improvised capacitor plates were connected to the electrometer. In an external magnetic field, the sample was polarized due to the magnetoelectric effect, and an uncompensated electric charge appeared on the sample surface, which was registered by an electrometer (Keithley Instruments, Inc., Model 610R). This ME_H-measurement technique is still used nowadays with modern electrometers, for example, Keithley Instruments, Inc., Models 642[11] and 6517b.[12]

Among the methods described above for measuring the magnetoelectric effect, the quasi-static method for measuring the direct ME_H-effect has been the most widely used. To implement such measurements, it is sufficient to connect the sample by a two-wire circuit to an electrometer and apply an external magnetic field. The measured value of the electric charge on the sample surface can easily be interpreted as electrical polarization if its geometric dimensions are known. This method is the most direct and does not require calibration, in contrast to the Astrov method. However, having data only on the direct magnetoelectric effect, it is difficult to talk about the whole picture of the magnetoelectric interaction, since we only see one side of the coin, so recently more new publications about the reverse ME_E-effect have been published.[8,9,13]

In addition to the quasistatic method for measuring the ME_H-effect, the dynamic method developed by J.-P. Rivera[11] is also known. The peculiarity of this method lies in the fact that the measurements are carried out by applying simultaneously a constant and an alternating magnetic field. In this case, if the magnetoelectric polarization is described by two terms, linear and quadratic in the magnetic field, the resulting polarization oscillation at the frequency of the applied alternating magnetic field depends on the susceptibility of not only the linear term of the magnetoelectric effect but also the quadratic one. This applies equally to the ME_E-effect if the magnetization is described by linear and quadratic terms in the electric field. In this case, the change in magnetization due to the magnetoelectric effect is described by the expression

$$\Delta M = \alpha(H)E + \beta(H)E^2, \tag{1}$$

where ΔM is the magnetic moment variation in applied electric field E, and α and β are the magnetoelectric susceptibilities of the linear and quadratic ME_E-effect components, respectively.

Each ME_E-effect component can be determined separately using the lock-in detection method. In the applied sinusoidal ac electric field $E(t) = e \times \cos(\omega t)$, e is the field amplitude and the magnetoelectric effect takes the following form:

$$\Delta M(t) = \alpha e \cos(\omega t) + \beta e^2 \cos^2(\omega t). \tag{2}$$

Transforming Eq. (2), we obtain

$$\Delta M(t) = \frac{\beta e^2}{2} + \alpha e \cos(\omega t) + \frac{\beta e^2}{2}\cos(2\omega t). \tag{3}$$

The second and the third terms in Eq. (3), i.e., the first and second harmonics, respectively, can be measured separately by the synchronous detection method. Thus, we can determine the ME_E-effect susceptibilities

$$\alpha = \frac{\Delta M'}{e};\ \beta = \frac{2\Delta M''}{e^2}, \tag{4}$$

where $\Delta M'$ and $\Delta M''$ are the experimental magnetic moment oscillation amplitudes at frequencies ω and 2ω, respectively.

Let us now consider the case of an electric field containing both the ac and dc components: $E(t) = e_0 + e \times \cos(\omega t)$. Then, we obtain from Eq. (1),

$$\Delta M(t) = \left[\alpha e_0 + \beta\left(e_0^2 + \frac{e^2}{2}\right)\right] + e(\alpha + 2\beta e_0)\cos(\omega t) + \frac{\beta e^2}{2}\cos(2\omega t). \tag{5}$$

It can be seen from Eq. (5) that the second magnetoelectric effect term corresponding to the first harmonic of magnetic moment oscillations depends on the susceptibility of the quadratic contribution β in the presence of the dc component e_0. At the same time, at $e_0 = 0$, the first harmonic of the magnetoelectric effect is only determined by the linear term susceptibility α. The effective first harmonic susceptibility is

$$\alpha^* = \alpha + 2\beta e_0. \tag{6}$$

The dependence of the first harmonic of the magnetoelectric effect on the dc electric field value makes it possible to control the magnetoelectric effect value. It should be noted that the sign of the dc component e_0 can be either positive or negative; therefore, the magnetoelectric effect at the first harmonic can be either suppressed or amplified. This is highly promising for applications that require tuning of the magnetoelectric effect. In addition, this opens new opportunities for detecting the magnetoelectric effect quadratic term in the electric field by using only the first-harmonic detection.

Susceptibility, β, is expressed as

$$\beta = \frac{\Delta M' - \alpha e}{2ee_0}.$$

To determine susceptibility, β, two measurements are required: the detection of the first harmonic without the dc component of the applied electric field to determine susceptibility α and the measurement with the dc component e_0. A similar experiment, but aimed at detection of the ME_H-effect, was carried out by J.-P. Rivera in 1994.[11]

The aim of this study was to investigate the effect of the dc electric field component e_0 applied to a multiferroic on the value of the ME_E-effect. To carry out such an experiment, it is very appropriate to use the family of rare-earth iron borates. The compounds are known to show a large magnitude of the magnetoelectric effect. Moreover, we know of at least three rare-earth iron borates where a quadratic term is present in dependence of the magnetoelectric effect on the electric field: $SmFe_3(BO_3)_4$,[14] $NdFe_3(BO_3)_4$, and $HoFe_3(BO_3)_4$.

Among these three compounds, samarium iron borate is the most attractive since it does not undergo any structural phase transitions: the space group $R32$[15–17] remains unchanged down to 2 K.[18,19] Sm^{3+} ions occupy only the position with the point symmetry group D_3 and are surrounded by six O_2^- ions, which form a trigonal prism with the C_3 axis of symmetry parallel to the crystallographic axis c. The moments of Fe^{3+} ions become ordered in the ab plane below $T_N = 33$ K, as shown in the measurements of the temperature dependence of magnetic susceptibility[20] and the spectroscopic investigation of oriented $SmFe_3(BO_3)_4$ single crystals.[18] The easy plane character of the antiferromagnetic structure was supported by neutron scattering experiments performed on $SmFe_3(BO_3)_4$ powders.[19] In addition, samarium iron ferroborate is noteworthy for having a giant magnetodielectric effect in an external magnetic field.[21]

II. EXPERIMENT, RESULTS, AND DISCUSSION

A samarium iron borate $SmFe_3(BO_3)_4$ single crystal was grown by the solution–melt method using bismuth trimolybdate, i.e., 80 wt. % $(Bi_2Mo_3O_{12} + 2B_2O_3 + 0.6Sm_2O_3) + 20$ wt. % $SmFe_3(BO_3)_4$.[22] The saturation temperature of 960 °C of this molten solution was determined using probe crystals. At $T = 1050$ °C, a ring crystallizer with seed crystals was hung over the molten solution. The temperature was then decreased to the saturation temperature $T = T_{sat} + 10$ °C $= 970$ °C, at which the holder with the seed crystals was immersed in the molten solution and was then rotated at a rate of 30 rpm. After 15 min, the temperature was decreased to $T = T_{sat} - 7\,°C = 953\,°C$. The crystals were then grown during a computer assisted decrease in the temperature at an increasing rate of 1–3 K/day, which ensured a crystal growth rate of at most 1 mm/day. The grown single crystals were $5\times4\times3$ mm^3 in size and had good optical quality and natural faceting. A sample for investigations was cut in the form of a rectangular plate with a thickness of 0.78 mm and an area of ~4 mm^2.

As in Ref. 14, we use the orthogonal system of coordinates (x, y, z), where x and z coincide with the a and c crystallographic directions, respectively, and the y axis is perpendicular to the xz plane. To apply an electric field to the sample, its yz face was coated with conductive epoxy glue.

For the experiment, we used a handmade measuring device,[13,23] assembled using the Astrov method. Figure 1 shows a schematic representation of its appearance in a section. Sample 1 is connected via wires 2 to alternating (constant) voltage sources. When the magnetic moment is changed, a signal is generated in the pick-up coils 3 with the frequency of the applied alternating voltage ω (the first harmonic) or with a doubled frequency 2ω (the second harmonic), which is measured by the Stanford Research Systems SR830 lock-in amplifier. A temperature sensor 4 located near the sample is used for temperature control. An external magnetic field is created by a superconducting solenoid 5 (up to 80 kOe).

In the experiment, the dc electric field e_0 and exciting ac electric field $e\times\cos(\omega t)$ with a frequency of 1 kHz were applied simultaneously to the $SmFe_3(BO_3)_4$ single crystal. At the same time, the sample was in the dc magnetic field H. The detected quantities were amplitudes of the first ($\Delta M'$) and second ($\Delta M''$) harmonic oscillations of the magnetic moment, which correspond to the second and third terms of Eq. (5), respectively:

$$\Delta M'(t) = e(\alpha + 2\beta e_0)\cos(\omega t), \tag{7}$$

$$\Delta M''(t) = \frac{\beta e^2}{2}\cos(2\omega t). \tag{8}$$

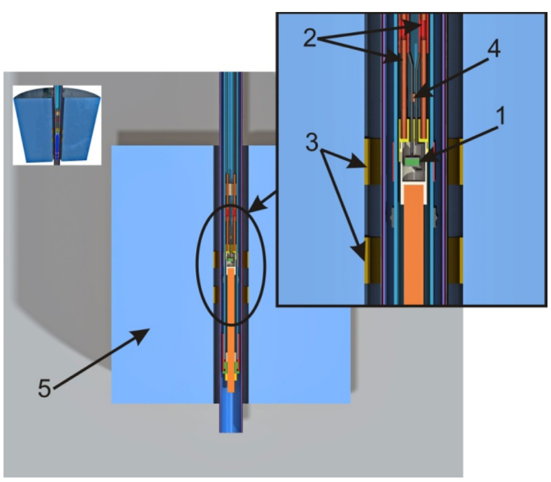

FIG. 1. Experimental setup for measuring the inverse ME_E-effect. 1: sample, 2: current-carrying wires for applying an electric field to the sample, 3: a pair of pick-up coils, 4: thermal sensor, and 5: superconducting solenoid.

Figure 2 shows the effective susceptibility $\alpha^* = d(\Delta M')/dE$ of the magnetoelectric effect at the first harmonic as a function of magnetic field H at different dc components e_0 of the electric field. It can be seen from Fig. 2(a) that the dc component e_0 of the external electric field exerts a significant impact on the magnetoelectric effect. In this case, the magnetic moment oscillations at frequency ω can be either amplified or suppressed, depending on the sign of the applied dc electric field e_0.

Figure 2(b) depicts the effect of field e_0 on the α^* value as the difference $\Delta\alpha = \alpha^* - \alpha$ between the ME_E-effect susceptibilities with and without applied field e_0. According to Fig. 2(b), in the applied electric fields e_0 with the same absolute value, but different signs, slight asymmetric α^* value variations are observed. This can be partially explained by the fact that the applied electric field e_0 also affects susceptibility β of the quadratic magnetoelectric effect term (Fig. 3). Figure 3 shows that, depending on the sign of applied field e_0, the maximum of the $\beta(H)$ dependence shifts toward stronger or weaker magnetic fields. The origin of such a behavior is still unclear, but taking into account that the investigated crystal is piezoelectric, the electric field can induce the strain responsible for the observed $\beta(H)$ shift due to the change in the crystal field and, consequently, the Stark structure of magnetic ions.

In addition, we attempted to detect the influence of the dc electric field e_0 on the magnetoelectric effect in paramagnetic holmium aluminum borate $HoAl_3(BO_3)_4$. However, the

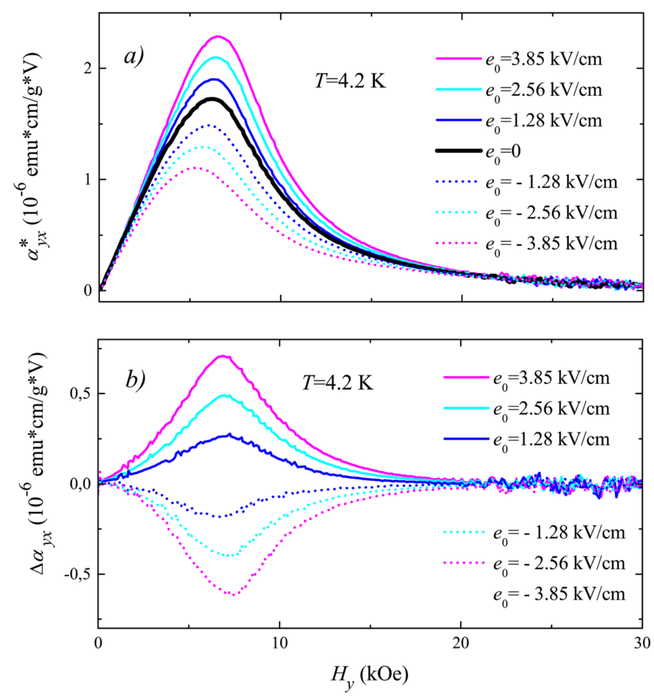

FIG. 2. (a) Effective susceptibility α^* of the ME_E-effect measured at the exciting ac electric field frequency ω versus magnetic field H_y at different dc electric fields e_0 and $T = 4.2$ K. (b) Difference $\Delta\alpha = \alpha^* - \alpha$ between the susceptibilities measured in the applied dc field e_0 and without it versus external magnetic field H_y at $T = 4.2$ K.

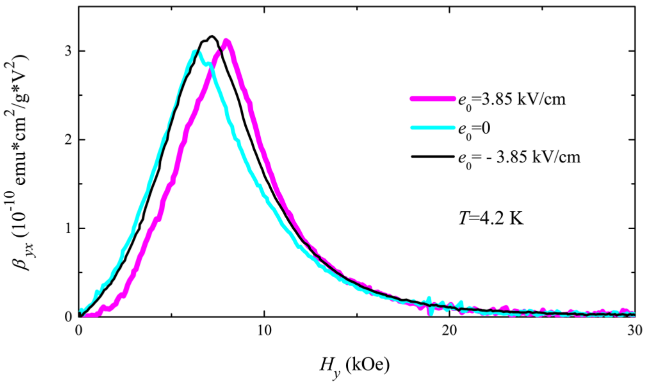

FIG. 3. Dependence of susceptibility β of the quadratic ME_E-effect component on external magnetic field H at different dc electric field components e_0. $T = 4.2$ K.

experiment did not reveal any changes in the ME_E-effect in this compound. There is no second harmonic of the ME_E-effect in holmium aluminum borate ($\beta = 0$).

According to the above mathematics, the susceptibility of the magnetoelectric effect at the first harmonic at $e_0 \neq 0$ is determined as $\alpha^* = \alpha(0) + 2\beta e_0$, where $\alpha(0)$ is the susceptibility of the linear ME_E-effect component determined at $e_0 = 0$ and β is the susceptibility of the quadratic ME_E-effect component determined at the specified e_0 value. Using the obtained experimental $\alpha(0)$ and $\beta(e_0)$ values, we calculated the α^* values shown by dashed lines in Fig. 4. The experimental results are shown by solid lines in Fig. 4. The theoretical field dependence of the first harmonic of the ME_E-effect is in qualitative agreement with the obtained experimental result, but the quantitative estimation of the effect appeared to be too high. Particular attention should be paid to the lower dashed line in Fig. 4 in the portion where the α^* value changes its sign and becomes negative in certain magnetic fields. Due to the limitation imposed on the applied dc electric field e_0 value, we could not experimentally detect this phenomenon; it is only reflected in theoretical dependence. Nevertheless, we assume this effect to be quite attainable; in practice, it suggests the change in the magnetic moment oscillation phase by π; i.e., at $\alpha^* > 0$, the signal is antiphase to the signal at $\alpha^* < 0$.

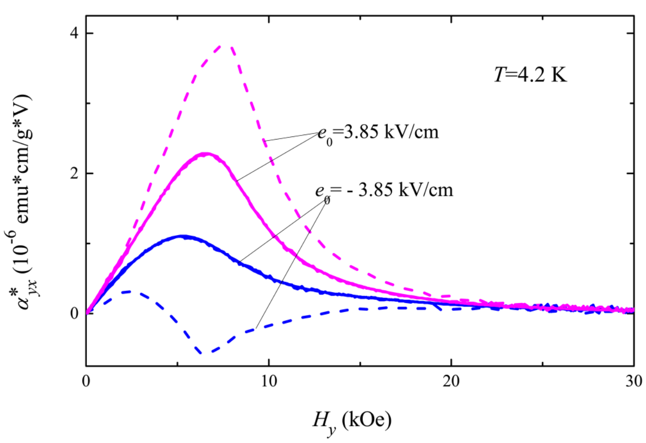

FIG. 4. Theoretical and experimental magnetic-field dependences of effective susceptibility α^* (dashed and solid lines, respectively) at different dc electric fields e_0. $T = 4.2$ K.

If the magnetoelectric effect in a sample is only determined by the quadratic component ($\alpha = 0$, $\beta \neq 0$), the simultaneously applied dc and ac electric fields yield the effective first-harmonic susceptibility α^* in the form $2e_0e$. In this case, the dc component of e_0 can be considered as a trigger, which switches the magnetic moment oscillation phase by π via changing the e_0 sign. This is interesting for technological applications.

III. CONCLUSIONS

Thus, we investigated the effect of the dc component e_0 of the external electric field applied against the background of the exciting ac field $e \times \cos(\omega t)$ on the inverse ME_E-effect in the samarium iron borate $SmFe_3(BO_3)_4$ single crystal. In the investigated compound, the magnetoelectric effect includes the linear and quadratic components, which results in the presence of both the first and second harmonics of the ME_E-effect upon excitation by an ac field. The experiment showed that, indeed, the dc component e_0 affects the ME_E-effect detected at the excitation frequency ω. At the same time, it exerts almost no impact on the second harmonic of the ME_E-effect detected at 2ω. A mathematical model was proposed, which explains the behavior of the first harmonics, but agrees only qualitatively with the experimental data.

Our experiment demonstrated the possibility of controlling the first harmonic of the magnetoelectric effect when there are both linear and quadratic ME_E-effect components. This can be interesting for future technological applications.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, projects no. 17-32-50043_mol_nr and no. 18-02-00696_a.

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