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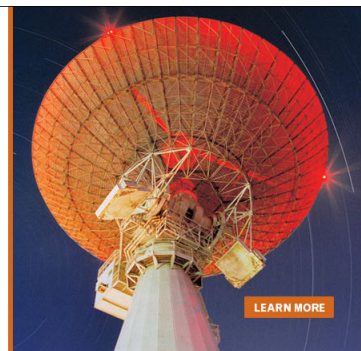Appl. Phys. Lett. **84**, 3516 (2004); 10.1063/1.1739277

Magnetostrictive and magnetoelectric behavior of Fe−20 at.% Ga/Pb(Zr,Ti)O$_3$ laminates

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The magnetostrictive and magnetoelectric (ME) properties of laminate composites of Fe−20 at.% Ga and Pb(Zr,Ti)O$_3$ (PZT) have been studied for laminates of different geometries. The results show that (i) a long-type magnetostrictive Fe−20 at.% Ga crystal plate oriented along $\langle 001 \rangle_c$ and magnetized in its longitudinal (or length) direction has higher magnetostriction than a disk-type one; and consequently (ii) a long-type Fe−20 at.% Ga/PZT laminate has a giant ME effect, and is sensitive to low-level magnetic fields. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1899247]

I. INTRODUCTION

Magnetostriction occurs in most ferromagnetic materials. Rare-earth systems, such as $Tb_{0.3}Dy_{0.7}Fe_2$, exhibit a giant Joule magnetostriction at relatively low magnetic biases.[1] However, these rare-earth materials are expensive. It is also commonly known that ordinary Fe has a small magnetostrictive strain $(3/2)\lambda$, on the order of 30 ppm. However, the introduction of Ga into crystalline solution with Fe results in a significant enhancement of its magnetostriction, $(3/2)\lambda_{100} \approx 250$ ppm, as long as the distorted $A2$ (bcc α-Fe) phase remains stable—even though Ga reduces the spin density of the solution, it enhances its magnetostriction. Recently, a number of investigations have focused on Fe–Ga (Galfenol) alloys due to the combination of its high mechanical strength, good ductility, relatively large $(3/2)\lambda_{100}$ values, low saturation fields, high blocking stress, and low cost.[2–7] Galfenol has potential applications in acoustic projectors, acoustic sensors, and actuators.[8,9]

Magnetoelectric materials have been very interesting since early Swiss[10] and Russian[11] work, and have recently had a renaissance (now commonly called multiferroic) in Nature, Science, Phys. Rev. Lett.,[12–16] and other high-impact journals. The magnetoelectric (ME) effect is a polarization P response to an applied magnetic field H, or conversely a magnetization M response to an applied electric field E. Previously, ME effects have been reported in composites of piezoelectric Pb(Zr,Ti)O$_3$ (PZT) or Pb(Mg$_{1/3}$Nb$_{2/3}$O$_3$−PbTiO$_3$) (PMN–PT) layers laminated with magnetostrictive $Tb_{1-x}Dy_xFe_{2-y}$, Permendur, Ni$_{1-x}$Co$_x$Fe$_2$O$_4$ (NFO), or Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ (CFO) ones.[17–29] In this article, we will show that laminate composites of magnetostrictive Fe−20 at.% Ga crystals and piezoelectric PZT ceramics also have a large ME coupling. Neither material is itself "magnetoelectric;" however, a large ME product property results from the elastic interaction of magnetostric-tive and piezoelectric layers. Furthermore, Fe–Ga alloys have the advantages of low saturation fields, relatively high magnetostriction, and low costs. These features offer Fe–Ga/PZT ME laminates potential in magnetic field and electric current sensing applications.

II. MAGNETOSTRICTION AND ME COUPLING MODES

A. Magnetostrictive vibrational modes

Similar to magnetostrictive $Tb_{1-x}Dy_xFe_{2-y}$ (Terfenol-D) materials, the magnetostrictive strain of Fe–Ga crystals is anisotropic, depending significantly upon the direction along which a magnetic field H is applied. Consequently, Fe–Ga crystals can have large magnetostrictive effects only when operated in particular modes. In addition, the magnetostrictive response of a Fe–Ga crystal to an applied H is also related to the crystal's shape and size. However, for a given shape/size, there is a principal magnetostrictive direction along the maximum dimension direction of the sample. Along this direction, the magnetostrictive strain is a maximum. Correspondingly, the magnetostrictive strain (or vibration) along this direction is defined as the principal strain (or vibration) mode. When H is applied parallel to the principal direction, the Fe–Ga crystal can be said to be operated in its longitudinal (or L) mode; whereas when H is applied perpendicular to this direction, it is designated as a transverse (or T) mode. As will be shown later in this article, L-mode long-type Fe–Ga crystal plates have larger magnetostrictive strains under smaller applied magnetic fields, than the T-mode ones.

B. Magnetoelectric coupling modes

In laminate composites, such as the three-layer Fe−20 at.% Ga/PZT/Fe−20 at.% Ga one of this investigation, the layers of the bimaterial are stress coupled. When the magnetostrictive layers are strained under H, the piezoelectric layers will undergo forced oscillation. Consequently, an electric field E (or voltage) is induced across the piezo-

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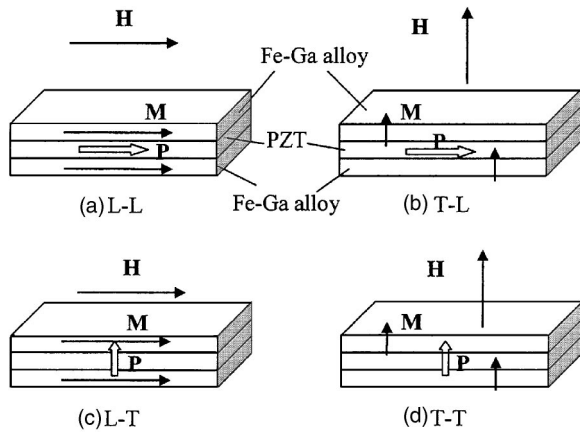[a]Author to whom correspondence should be addressed; electronic mail: sdong@mse.vt.edu

FIG. 1. Schematic illustration of the various ME coupling modes used in this investigation: (a) $L-L$; (b) $T-L$; (c) $L-T$; and (d) $T-T$.

electric layer due to piezoelectricity. This elastically coupled response between an applied H and an induced E (or vice versa) is known as the magneto-(elasto)-electric (or ME) effect of the laminate. The various modes studied in this investigation are illustrated in Fig. 1. When both the applied H and the induced E are parallel to the principle vibration mode, the ME laminate can be said to operate in its $(L-L)$ mode [see Fig. 1(a)]. When the applied H is perpendicular to the principle mode and the induced E parallel to it, the ME laminate operates in its $(T-L)$ mode [see Fig. 1(b)]; whereas, when H is applied parallel to the principle direction and the induced E measured perpendicular to it, the laminate operates in its $(L-T)$ mode [see Fig. 1(c)]. Finally, when both the applied H and induced E are perpendicular to the principle mode, the laminate operates in its $(T-T)$ mode [see Fig. 1(d)].

Magnetoelastic and elastic–electric equivalent circuits that are similar to those of Terfenol-D/PZT laminate composite[19,20] can also be used to describe the ME coupling of Fe–20%Ga/PZT laminates operated in either $L-L$ or $L-T$ modes. Accordingly, the $L-T$ mode $|dV/dH_3|_{(L-T)}$ and $L-L$ mode $|dV/dH_3|_{(L-L)}$. ME voltage coefficients can be derived by an equivalent circuit analysis; however, many material parameters for Fe–Ga crystals remain unknown in this material.

III. EXPERIMENTAL PROCEDURE

Crystals of Fe–20 at. % Ga were grown by a Bridgman method at Ames Laboratory. The crystals were cut into rectangular plates of dimensions $12.7 \times 6 \times 1$ mm^3, or disk plates of a diameter 12.7 mm and a thickness 1 mm. All Fe–20 at. % Ga crystals were oriented along the $\langle 001 \rangle_c$ direction. The crystals were annealed at 1100 °C for 168 h, using heating and cooling rates of 10 °C/min, after which they were considered to be in the "slow-cooled" state. Both soft-type piezoelectric Pb(Zr, Ti)O$_3$ (PZT) with high d-type piezoelectric constants but low mechanical quality factor Q_m, and hard-type PZT with low piezoelectric constants but high Q_m were used for ME laminates.

Three-layer long-type Fe–20 at. % Ga and PZT laminates were prototyped by (i) sandwiching one longitudinally

poled rectangular PZT plate (soft or hard type, sizes: $14 \times 6 \times 1$ mm^3) between two longitudinally magnetized Fe–20 at. % Ga ones, i.e., $(L-L)$ mode laminates (prototype No. 1 made of soft PZT, and prototype No. 2 made of hard); and (ii) sandwiching one transversely poled rectangular PZT plate (soft or hard, sizes: $14 \times 6 \times 0.5$ mm^3) between two longitudinally magnetized Fe–20%Ga ones, i.e., $(L-T)$ mode laminates (prototype No. 3 made of soft PZT, and prototype No. 4 of hard). The prototypes were laminated using epoxy resin, and were cured at 80 °C for 3–4 h under load. These configurations are similar to prior ME modes in Terfenol-D/PZT[17] and CFO–NFO/PZT[15,18] laminates. The static capacitance of the transversely poled PZT layers was 2.04 nF, whereas that of longitudinally poled PZT layers was only 0.036 nF. Figure 1 illustrates the laminate configurations of various operational modes.

The magnetostriction of the Fe–20 at. % Ga layers and Fe–20 at. % Ga/PZT laminated composites were measured, via a resistance strain-gauge method. The voltages induced across the two ends of the PZT layer in the Fe–20 at. % Ga/PZT laminate were measured for various dc magnetic biases (H_{dc}) and ac magnetic drives (H_{ac}) over the frequency range of $10^{-2} < f < 10^5$ Hz, using a charge amplifier combined with a phase-locking (i.e., lock-in) method. An electromagnet was used to apply dc magnetic bias H_{dc} and one pair of Helmholtz coils was used to generate a small H_{ac}, via an input current I_{coil}, which was superimposed on H_{dc}. Since the $L-L$ ME composite has a very low static capacitance, we found it necessary to use a charge amplifier to obtain correct induced ME voltages, as the distributed capacitance of the connecting cables and electronic meters could notably affect the measured values.

IV. RESULTS AND DISCUSSION

A. Magnetostriction of Fe−20 at. % Ga crystals

To determine an optimum magnetostriction mode, two types of $\langle 001 \rangle_c$ Fe−20 at. % Ga crystals plates—a long type and a disk type—were studied. These measurements clearly confirmed that an L-mode long-type Fe−20 at. % Ga crystal plate has larger magnetostriction at low magnetic fields. This is important in understanding the ME properties that will subsequently be presented in this article. Accordingly, in our ME studies, we have focused on this long-type configuration.

Figure 2 shows the ε_m-H response for a long-type rectangular Fe−20 at. % Ga crystal plate. Data are shown for both the longitudinal (expansion) strain where H_{dc} is applied along the length of the rectangular Fe–Ga plate (i.e., L mode), and the transverse (contraction) strain where H_{dc} is applied along the thickness of the rectangular plate (i.e., T mode). Higher magnetostrictive strains at lower biases (0–700 Oe) were found when H was applied along the longitudinal direction, relative to the transverse. The longitudinal magnetostrictive strain of a Fe−20 at. % Ga crystal plate was 330 ppm at $H_{dc}=700$ Oe, whereas the transverse one was only 5 ppm. At lower H_{dc}, the L-mode magnetostriction is a factor of $\sim 60\times$ higher, than that of the T mode. However, for $H>700$ Oe, the magnetostriction of the L mode saturated; whereas that of the T mode did not saturate until
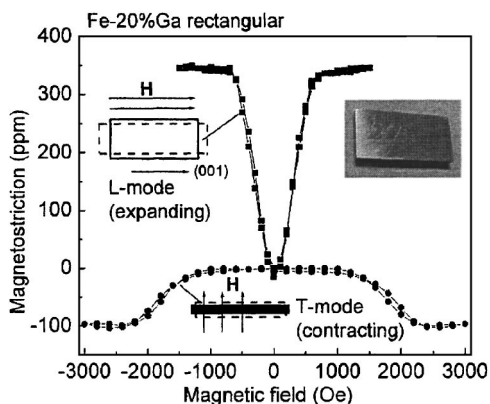
FIG. 2. Magnetostrictive strains of free $\langle 001 \rangle_c$ Fe–20 at. % Ga crystals of various geometries: (a) a rectangle of dimensions $12 \times 6 \times 1$ mm^3 and (b) a disk of diameter 12.7 mm and a thickness of 1 mm.

$H_{dc} > 2400$ Oe, where its induced strain reached a maximum of ~100 ppm. Relative to the L mode, the T mode has a higher demagnetization factor N; and consequently a higher magnetic field of ~2400 Oe is required to reach saturation. The insets of Fig. 2 illustrate a photo of a rectangular shaped Fe–20 at. % Ga crystal plate and the induced longitudinal and transverse shape changes. For H_{dc} applied longitudinally, the length of the rectangular plate expands and its thickness contracts; whereas for H_{dc} applied transversely, the length of the plate contracts and its thickness expands.

Figure 3 shows the ε_m–H response for a disk-type Fe–20 at. % Ga crystal plate. Data are shown for both a longitudinal (expansive) strain where H_{dc} is applied along the diameter of the disk (i.e., L mode), and a transverse (contractive) strain where H_{dc} is applied along the thickness of the disk (i.e., T mode). The maximum L-mode magnetostrictive strain of the disk-type plate was only 100 ppm at $H_{dc} = 1000$ Oe; whereas, the maximum T-mode strain of the disk was -100 ppm at $H_{dc} = 2300$ Oe. Again, relative to the rectangular type, the disk type has a higher demagnetization factor N; and thus a higher magnetic field of ~1000 Oe for L
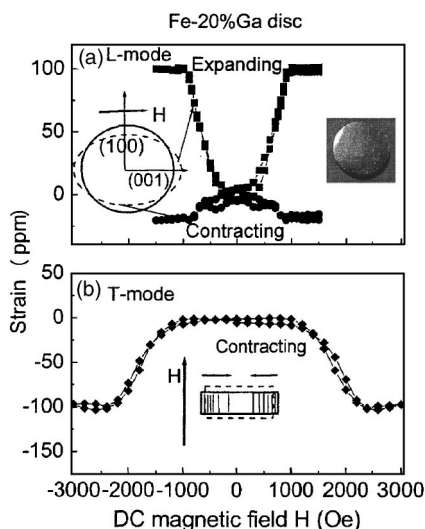

FIG. 3. Magnetostrictive strains of free rectangular type Fe–20 at. % Ga crystal plates (of dimensions $12.7 \times 6.0 \times 1.0$ mm^3) as a function of dc magnetic bias H_{dc}.
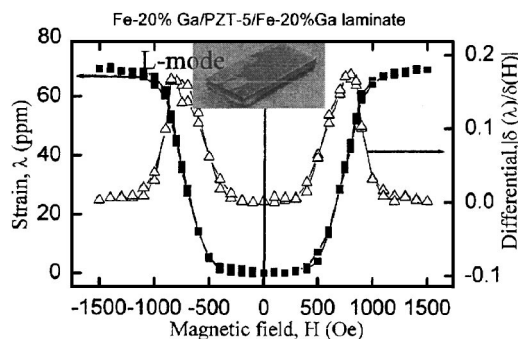

FIG. 4. Magnetostriction of Fe–Ga/PZT/Fe–Ga laminate as a function of H_{dc}, and its differential dependence on H_{dc}.

mode is required to reach saturation. However, their T modes have almost the same demagnetization factor N. Comparisons of the data in Figs. 2 and 3 will show that the magnetostrictive strain of the disk-type laminate is much lower than that of the long-type ones for $0 < H_{dc} < 1000$ Oe. The insets of Fig. 3 illustrate a photo of a disk-type Fe–20 at. % Ga crystal plate, and the induced longitudinal (diameter) and transverse (thickness) shape changes. For H_{dc} applied longitudinally, the disk-type crystals tend to become elliptical, and the thickness is decreased; whereas for H_{dc} applied in thickness direction, the thickness expands and the diameter is decreased.

B. Magnetostriction of Fe–20 at. % Ga/PZT laminates

The magnetostriction strain for a long-type Fe–20 at. % Ga/PZT composite was remeasured after lamination, using a resistance strain gauge. These measurements revealed a maximum magnetostrictive (expansion) strain along the laminate's length of ~70 ppm at a $H_{dc} = 1000$ Oe, as can be seen in Fig. 4. Comparisons of these data to those of the free condition (see Fig. 2) will reveal that lamination with PZT layers imposes a load to the Fe–20 at. % Ga layers which: (i) significantly decreases the magnetostrictive strain relative to that of the free condition of the crystal; (ii) lags the magnetostrictive response until 500 Oe; and (iii) shifts the maximum strain to a higher H_{dc}, presumably due to suppression of magnetic domain wall motion. Figure 4 also illustrates the differential of the magnetostrictive strain to an applied H_{dc}, which is a measure of the change in the effective piezomagnetic coefficients with H_{dc}. To obtain a large effective piezomagnetic coefficient (i.e., $\delta \varepsilon / \delta H$), these data show that a dc bias of $H_{dc} = 800$ Oe is required. Correspondingly, a similar bias of $H_{dc} \approx 800$ Oe will be needed to achieve optimum ME effects.

C. ME responses

Figure 5(a) shows the ME voltage coefficient for a long-type three-layer Fe–Ga/PZT/Fe–Ga laminate (prototype No. 1) as a function of H_{dc} for both L–L and T–L modes. The data in this figure were taken at a frequency of $f = 1$ kHz and a drive of $H_{ac} = 1$ Oe. The value of $\partial V_{ME}^{L,L} / \partial H$ can be seen to be strongly dependent on H_{dc}. The results show that the L–L mode of Fe–20%Ga/PZT laminates has a maximum ME effect of $\partial V_{ME}^{L,L} / \partial H \sim 345$ mV/Oe at a magnetic bias of H_{dc}

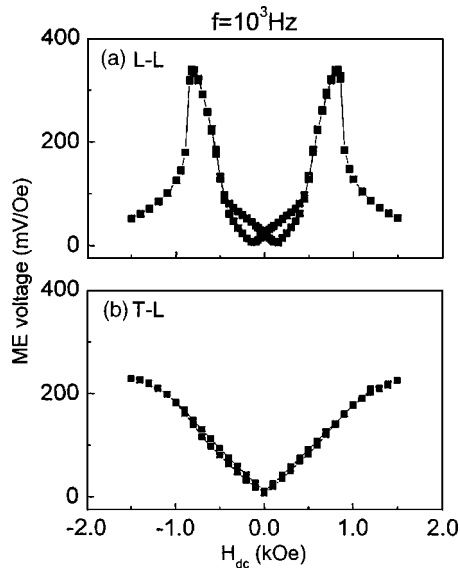FIG. 5. ME voltage coefficients of prototype No. 1 at $f=1$ kHz for various modes: (a) $L-L$ and (b) $T-L$.

FIG. 6. ME voltage coefficients of prototype No. 2 at $f=1$ kHz for various modes: (a) $L-T$ and (b) $T-T$.

$=800$ Oe, where the slope of the magnetostriction of the laminate shown in Fig. 4 is highest. For $H_{dc} > 800$ Oe, $\partial V_{ME}^{L,L}/\partial H$ decreased dramatically with increasing H_{dc}, as the Fe-20 at. % Ga layers of the laminate approached saturation of its magnetostriction. It is relevant to note that the maximum value of $\partial V_{ME}^{L,L}/\partial H$ that we report here for Fe–20%Ga/PZT laminates is close to that of $L-L$ configurations of Terfenol-D/PZT and Terfenol-D/PMN–PT ones,[24,26] even though the saturated magnetostriction (λ_s) of Fe–Ga is smaller than that of Terfenol-D. This demonstrates that Fe-20 at. % Ga has comparably magnetoelastic coupling as that of Terfenol-D, under moderate magnetic fields. A long-type laminate favors the optimum combination of magnetostrictive and piezoelectric effects; in particular, the longitudinal magnetostrictive strain of Fe-20 at. % Ga, and the longitudinal piezoelectric strain of PZT are higher than the corresponding transverse ones. For the $T-L$ mode, we also observed a relatively large ME voltage coefficient of ~ 220 mV/Oe at a notably higher dc magnetic bias of $H_{dc} = 1500$ Oe, as shown in Fig. 5(b).

In addition, it is relevant to note that the value of the transverse magnetostriction for a free Fe-20 at. % Ga crystal was quite low for $H_{dc} < 1000$ Oe. However, when this same crystal was laminated to form a ME composite and operated in a T mode, a relatively large ME voltage coefficient of ~ 220 mV/Oe was still observed. This indicates that there is another factor influencing the ME coupling, presumably the elasto–electric coupling factor. This possibility is supported by reports[30] of increases in effective piezoelectric constants under uniaxial stress, which could enhance elastic–electric coupling, consequently increasing the ME output voltage.

For comparisons, Fig. 6 shows the ME voltage coefficients (prototype No. 3) for both the $L-T$ and $T-T$ modes as a function of H_{dc}. This data were also taken at a frequency of $f=1$ kHz and a drive of $H_{ac}=1$ Oe. The measured value of the ME voltage coefficients can be seen to be ~ 33 and
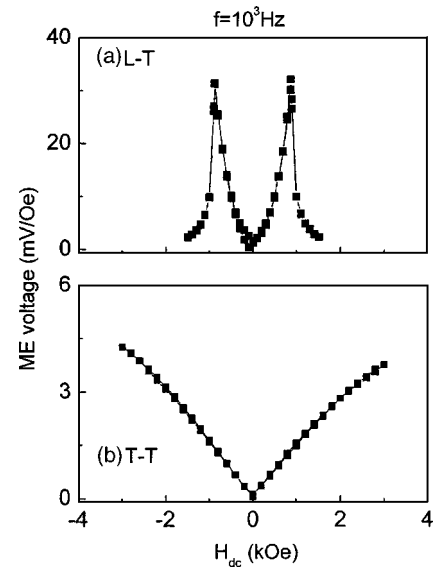
~ 4 mV/Oe for the $L-T$ and $T-T$ modes, respectively. This is a factor of $\sim 10\times$ smaller than that of the $L-L$ mode. However, the corresponding ME field coefficient was larger for the $L-T$ mode $[(\partial E_{ME}^{L,T}/\partial H)=640$ mV/cm Oe], relative to that of the $L-L$ mode $[(\partial E_{ME}^{L,L}/\partial H)=272$ mV/cm Oe].

D. ME sensitivity

Low-level magnetic field responses of the Fe–Ga/PZT laminate (prototype No. 1) operated in the $L-L$ mode are shown in Fig. 7. It can be seen that the induced ME voltage is a near linear function of H_{ac}. In this figure, the induced ME voltage can be seen to have a good linear response to H_{ac} over a wide field range from 10^{-9} T (or 10^{-5} Oe) to $\sim 10^{-3}$ T (or 10 Oe). These results demonstrate that our Fe–Ga/PZT laminate is quite sensitive to minute magnetic field variations. Further sensitivity improvements should be possible by replacing the PZT layers in the laminate with PMN–PT single crystal ones, which have significantly higher piezoelectric coefficients.[26]
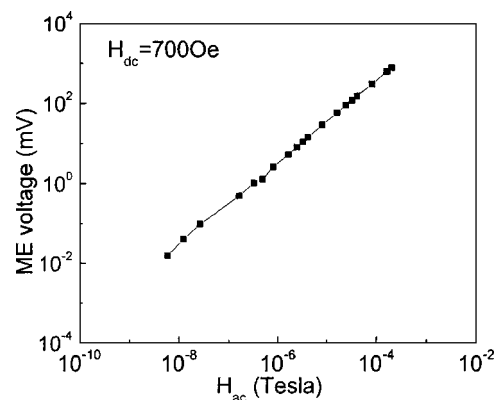

FIG. 7. Illustration of the magnetic field sensitivity. The induced ME voltage for prototype No. 1 under a $H_{dc}=750$ Oe and a measurement frequency of $f=1$ kHz as a function of ac magnetic field over the range of $10^{-9} < H_{ac} < 10^{-3}$ T.
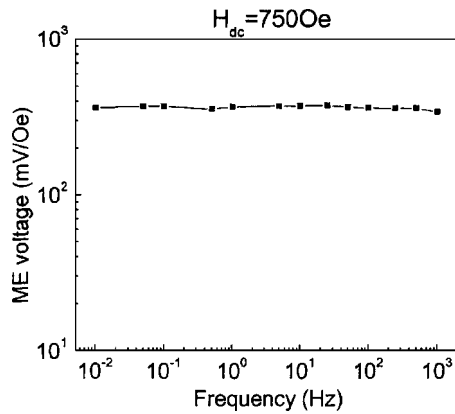
FIG. 8. Induced ME voltage for prototype No. 1 as a function of the ac magnetic drive frequency in low-frequency ranges of $10^{-2} < f < 10^3$ Hz; These data were taken using a $H_{dc} = 750$ Oe and $H_{ac} = 1$ Oe.

E. Frequency dependence of ME response

The frequency dependence of the induced ME voltage for the Fe–Ga/PZT laminates was then measured over a wider frequency range of $10^{-2} < f < 10^5$ Hz. The results show that the Fe–Ga/PZT laminate (prototype No. 1) has a very flat frequency response in the low-frequency range of $10^{-2} < f < 10^3$ Hz, as can be see in Fig. 8.

Upon approaching the natural resonance frequency, the induced ME voltage for both $L-L$ and $L-T$ modes was significantly enhanced, as shown in Fig. 9. The maximum ME voltage coefficient at resonance ($f_0 \sim 92.5$ kHz) for the $L-L$ mode (prototype No. 2) was ~ 7.24 V/Oe (or correspondingly 5.7 V/cm Oe for the field coefficient); whereas, for the $L-T$ mode (prototype No. 4), it was ~ 3.3 V/Oe (or correspondingly 66 V/cm Oe) at a resonance frequency of $f_0 = 96$ kHz. Clearly, the ME voltage coefficients at resonance are $\sim 20-100 \times$ higher than those at subresonant conditions. (Note that the resonance frequencies for the $L-L$ and $L-T$ modes are different because their magnetostrictive layer thickness ratios are different, resulting from a difference in their mean acoustic velocities.[24]) Although at low frequencies ME laminates of hard PZT layers have lower induced

ME voltages than those with soft ones, the opposite is true under resonant conditions—i.e., laminates of hard PZT have higher ME coefficients near f_0. This is because hard PZT has a higher mechanical quality factor Q_m than soft types. These values of ME voltage coefficients achieved from Fe–Ga/PZT laminates are comparable to, or slightly higher than, previous reports for Terfenol-D/PZT and CFO–NFO/PZT laminates.[17–29]

V. SUMMARY

In summary, a long-type magnetostrictive Fe–20 at. % Ga crystal plate has been found to have a higher magnetostrictive strain at lower fields, than a disk-type one. Furthermore, this long-type laminate of Fe–20%Ga and PZT has been found to have: (i) a large $L-L$ ME voltage coefficient of $\partial V_{ME}^{L,L}/\partial H > 345$ mV/Oe under modest dc magnetic biases; (ii) a dramatic enhancement in the ME response near the resonance frequency; and (iii) a high sensitivity to minute magnetic field variations. These results demonstrate the feasibility of fabricating low-cost, highly-sensitive magnetic field and/or electric current sensors using Fe–20 at. % Ga/PZT laminates.
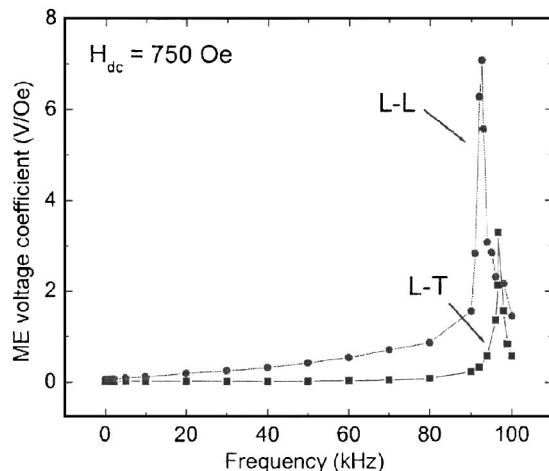
FIG. 9. Induced ME voltages for prototype Nos. 3 and 4 as a function of the ac magnetic drive frequency near the resonance frequency for $1 < f < 100$ kHz. These data were taken using a $H_{dc} = 750$ Oe and $H_{ac} = 1$ Oe.

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