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Logarithmic frequency dependence of the piezoelectric effect due to pinning of ferroelectric-ferroelastic domain walls

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Pinning of the ferroelastic-ferroelectric domain walls on randomly distributed defects in ferroelectric ceramics leads to a field dependence of the piezoelectric coefficient that is analogous to the Rayleigh law for magnetic susceptibility. It is shown in this paper that the piezoelectric coefficient of a lead zirconate titanate ferroelastic-ferroelectric system depends linearly on the logarithm of the frequency of the field. Both the reversible and irreversible components of the piezoelectric coefficient are found to be frequency dependent. A similar type of frequency dependence due to domain-wall pinning has been predicted for the magnetic susceptibility in disordered ferromagnets and dilute antiferromagnets. The presented results offer experimental evidence that the theoretical approach developed for domain-wall pinning effects in magnetic materials is generally valid for pinning processes in all ferroic systems, ferromagnetics, ferroelectrics, and ferroelastics. [S0163-1829(97)50502-9]

Effects of the domain-wall pinning (or more generally, pinning of moving interfaces) on magnetic and dielectric properties have been of substantial interest for many years. An example is the contribution to the magnetic susceptibility from interaction of the domain walls with randomly distributed pinning centers in disordered ferromagnets.[1,2] Several other examples and a detailed theoretical consideration of the problem may be found in work by Nattermann *et al.*[1] The theoretical treatment of the domain-wall pinning in magnetic systems has led to two general results. One is the field dependence of the magnetic susceptibility, χ, in the form of the classical Rayleigh law:[2,3]

$$\chi(H)=\chi_{\mathrm{init}}+\nu H, \tag{1}$$

where χ_{init} is the reversible component of the susceptibility, ν is the Rayleigh coefficient, and H is the magnetic field. The irreversible, field-dependent component of the susceptibility, νH, is due to domain-wall pinning and is responsible for weak-field hysteresis. The other important result is the logarithmic dependence of the susceptibility on frequency ω of the field:[1,4]

$$\chi(\omega)\sim\left[\frac{1}{\omega t_0}\right]^{\Theta}, \tag{2}$$

where exponent Θ is related to the roughness of the interface[1] and t_0 is a time constant.

Although magnetic systems (ferromagnets, antiferromagnets, and spin glasses) are most often treated in the literature, mechanisms of the domain-wall pinning should, as pointed out by Nattermann *et al.*, be similar in other physically equivalent systems, including ferroelectrics. This was recently confirmed by showing experimentally that the weak-field displacement of ferroelastic-ferroelectric domain walls in ferroelectric ceramics leads to field dependence of the longitudinal piezoelectric coefficient which is identical to the Rayleigh law.[5] That study suggests that the Rayleigh law is universal and valid for pinning effects of all types—ferromagnetic, ferroelastic, and ferroelectric—of ferroic domains. In the present paper, this result is extended to show that a relation analogous to Eq. (2) is valid for a piezoelectric response of a ferroelectric system. This result indicates that theoretical predictions[1,4] for the frequency dependence of domain-wall pinning processes in magnetic materials are also valid for pinning of ferroelectric-ferroelastic domain walls. It is further shown that the frequency dependence of

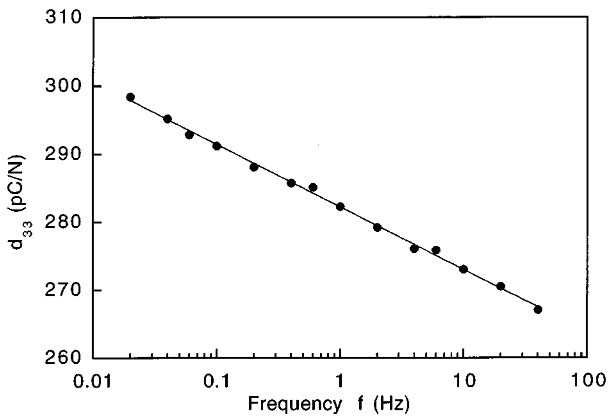

FIG. 1. The longitudinal d_{33} piezoelectric coefficient of PZT-Nb as a function of the frequency of ac pressure, at ~3 MPa amplitude of ac pressure. The solid line is the best fit to Eq. (3).

the piezoelectric coefficient is due to logarithmic frequency dependence of both reversible and irreversible components of the piezoelectric coefficient. Finally, it is shown that in the case of the piezoelectric coefficient, the exponent of the logarithmic term is ~1.

The direct d_{33} longitudinal piezoelectric coefficient of a soft lead zirconate titanate ceramic is measured by a method described in more detail in Ref. 5. Composition of the ceramic is $Pb(Zr_{0.52}Ti_{0.48})_{0.975}Nb_{0.025}O_3$ (PZT-Nb). Information on sample preparation and poling may be found in Ref. 5. The composition lays on the morphotropic phase boundary between rhombohedral and tetragonal phases which coexist in the ceramic due to local variations in the composition of the solid solution. The grains of the ceramic contain three types of piezoelectrically active non-180° domain walls: 109° and 71° walls in the rhombohedral phase and 90° walls in the tetragonal phase. These domain walls are simultaneously ferroelectric and ferroelastic walls. The ferroelectric-paraelectric phase transition of this composition is at 650 K.

The piezoelectric coefficient is first measured as a function of the frequency of ac pressure, at ac pressure amplitude ~3 MPa. The results are shown in Fig. 1. The piezoelectric

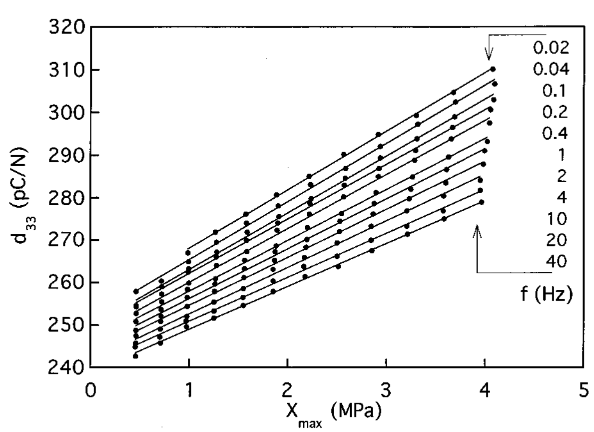

FIG. 2. The longitudinal d_{33} piezoelectric coefficient of PZT-Nb as a function of the amplitude of ac pressure, at different frequencies. The solid lines are best fits to Eq. (4), with fit parameters plotted in Fig. 3. All measurements were made under an external dc bias pressure of 19 MPa.

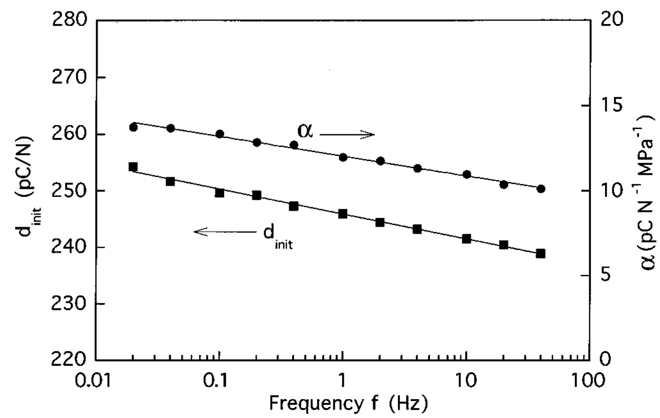

FIG. 3. The reversible and irreversible Rayleigh parameters, d_{init} and α, of d_{33} of PZT-Nb, as a function of the frequency of ac pressure. The solid lines are best fits to Eqs. (5) and (6), with fit parameters shown in the text.

coefficient decreases monotonically with the logarithm of the frequency and may be well represented with the linear equation

$$d_{33}(\omega)=F_0+F\ln\left(\frac{1}{\omega}\right), \quad (3)$$

where $F_0=289.6\pm0.1$ pC/N and $F\approx4.00\pm0.01$ pc/N. The uncertainties include only linear regression errors. The linear correlation factor R is 0.9987, and it may be concluded that the exponent of the logarithmic term is ~1. The piezoelectric coefficient shows the same type of frequency dependence as predicted for magnetic susceptibility in (anti)ferromagnets due to domain-wall pinning.[1,4]

It is next shown that the frequency dependence (3) of the piezoelectric coefficient is due to frequency dependence of both reversible and irreversible Rayleigh parameters for the piezoelectric effect. As discussed in detail in Ref. 5, weak-field dependence of the piezoelectric coefficient of ferroelectric ceramics may be described by a relationship analogous to the Rayleigh law (1):

$$d_{33}(X_{max})=d_{init}+\alpha X_{max}, \quad (4)$$

where d_{init} and α are reversible and irreversible Rayleigh parameters[2,3] for the piezoelectric effect, and X_{max} is the amplitude of ac pressure.

The piezoelectric coefficient is measured as a function of X_{max} at frequencies ranging from 0.02 to 40 Hz. Results are shown in Fig. 2. As expected, for each frequency, d_{33} vs X_{max} may be written in the form of the Rayleigh relationship (4). It is clear from Fig. 2 that d_{init} and α depend on the frequency of the ac field. α and d_{init} are calculated for each frequency by fitting the data in Fig. 2 with the Rayleigh relation (4). The results are shown in Fig. 3. Both reversible and irreversible Rayleigh parameters show a linear dependence with $\ln(1/\omega)$, and can be expressed as

$$d_{init}(\omega)=d_0+d\ln\left(\frac{1}{\omega}\right), \quad (5)$$

$$\alpha(\omega)=a_0+a\ln\left(\frac{1}{\omega}\right), \quad (6)$$

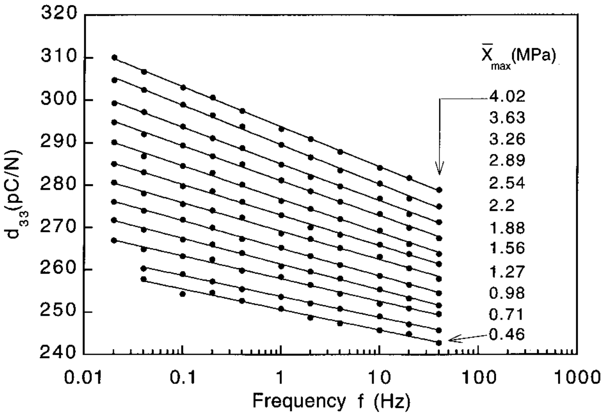

FIG. 4. The longitudinal d_{33} piezoelectric coefficient of PZT-Nb as a function of the frequency of ac pressure, at different amplitudes of the average ac pressure $\bar{X}_{max}$. Because for each pressure level in Fig. 2 X_{max} varies slightly with frequency, the average values of X_{max} for each pressure level in Fig. 2 are taken to generate plots for this figure. The solid lines are best fits to Eq. (9), with fit parameters shown in Fig. 5.

where $d_0=249\pm1$ pC N^{-1}, $d=1.9\pm0.2$ pC N^{-1}, $a_0=12.9\pm0.5$ pC N^{-1} MPa^{-1}, and $a=0.50\pm0.05$ pC N^{-1} MPa^{-1}. Errors in each linear regression analysis step are very small (the linear correlation coefficients $R>0.994$). Indicated uncertainties are estimated accumulated errors from all fitting steps.

The Rayleigh law (4) for the piezoelectric coefficient can be written in the following form, with frequency-dependent parameters:

$$d_{33}(\omega,X_{max})=d_{init}(\omega)+\alpha(\omega)X_{max}. \tag{7}$$

By inserting Eqs. (5) and (6) into Eq. (7), one obtains

$$d_{33}(\omega,X_{max})=D_0(X_{max})+D(X_{max})\ln\left(\frac{1}{\omega}\right), \tag{8}$$

where $D_0(X_{max})=d_0+a_0X_{max}$ and $D(X_{max})=d+aX_{max}$. Therefore, it follows from the Rayleigh law (4) and the frequency dependence of the Rayleigh parameters (5) and (6), that for a given ac field, the piezoelectric coefficient decreases linearly with logarithm of the frequency of field.

For completeness, it is next shown that the Rayleigh law may likewise be derived from the frequency dependence of the piezoelectric coefficient. Data shown in Fig. 2 are represented in Fig. 4 as d_{33} vs the logarithm of ω, for each amplitude of the ac pressure. As seen from Fig. 2, at each level of the ac pressure, X_{max} slightly changes as the driving frequency is varied. The pressures indicated in Fig. 4 are the average values ($\bar{X}_{max}$) over all examined frequencies. The largest error introduced by taking the average amplitude of ac pressure is about 1.9% for $\bar{X}_{max}=4.02$ MPa. For simplicity, $\bar{X}_{max}$ is hereafter written as X_{max}.

For each X_{max}, d_{33} decreases linearly with $\ln(1/\omega)$, and can be written as

$$d_{33}(\omega,X_{max})=G_0(X_{max})+G(X_{max})\ln\left(\frac{1}{\omega}\right), \tag{9}$$

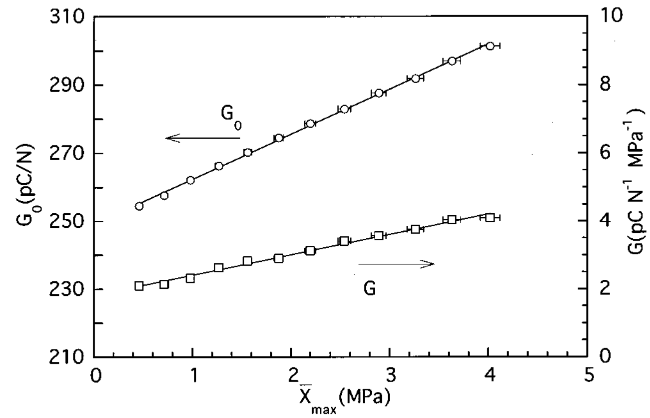

FIG. 5. Parameters G_0 and G of d_{33} vs $\ln(1/\omega)$ curves in Fig. 4, as a function of the amplitude of ac pressure. The error bars indicate error due to averaging of the pressure amplitude as explained in the text and in the caption for Fig. 4. The solid lines are best fits to Eqs. (10) and (11), with fit parameters shown in the text.

where G_0 and G are parameters which depend on X_{max}. G_0 and G are calculated for each pressure by fitting the data in Fig. 4 with Eq. (9). Both parameters depend linearly on pressure, as shown in Fig. 5, and may be written as

$$G_0(X_{max})=g_0+f_0X_{max}, \tag{10}$$

$$G(X_{max})=g+fX_{max}, \tag{11}$$

where $g_0=249\pm1$ pC N^{-1}, $f_0=13.2\pm0.4$ pC N^{-1} MPa^{-1}, $g=1.8\pm0.2$ pC N^{-1}, and $f=0.59\pm0.02$ pC N^{-1} MPa^{-1}. The indicated uncertainties include estimated accumulated errors from successive fitting steps and the error introduced by averaging the amplitude of the ac pressure. By inserting Eqs. (10) and (11) into Eq. (9) one obtains

$$d_{33}(\omega,X_{max})=d^G_{init}(\omega)+\alpha^G(\omega)X_{max}, \tag{12}$$

where $d^G_{init}(\omega)=g_0+g\ln(1/\omega)$ and $\alpha^G(\omega)=f_0+f\ln(1/\omega)$. Equation (12) has the form of the Rayleigh law (4), with frequency-dependent parameters. By comparing coefficients in Eqs. (5) and (6) and (10) and (11), it follows that $\alpha\approx\alpha^G$, $d_{init}\approx d^G_{init}$, $D_0\approx G_0$, and $D\approx G$. Therefore, under the conditions where Eqs. (5) and (6) and (10) and (11) are valid, the classical Rayleigh relationship (7) may be derived from Eq. (9), and vice versa. Equations (7) and (9) are two representations of the same relationship.

The logarithmic frequency dependence of d_{33} is thus shown to be due to the frequency dependence of *both* the reversible and irreversible Rayleigh parameters. It is interesting that Prejean and Souletie[3] have shown that in the CuMn spin glass, the reversible component of the magnetic susceptibility (χ_{init}) is proportional to $\ln(t)$, where t is the measurement time. The same temporal dependence was observed by Leitao *et al.*[6] for the quadratic (irreversible) component of thermoremanent magnetization in the $Fe_{0.7}Mg_{0.3}Cl_2$ antiferromagnet. Moreover, Leitao*et al.* have shown experimentally that the exponent of the logarithmic term in $Fe_{0.7}Mg_{0.3}Cl_2$ is $\sim$1. This is in disagreement with the theoretically predicted value[6] but agrees with the value of the exponent which is obtained experimentally for d_{33} in the present work. The value of the exponent is not discussed in this paper, however, it has been a subject of several studies in the past and may be of particular importance for testing the results of theoretical models of interface pinning.[1,6,7]

In conclusion, it is shown that the pinning of ferroelectric-ferroelastic domain walls in a ferroelectric system has the similar effect on the field and frequency dependence of the piezoelectric coefficient, as the pinning of magnetic domain walls has on susceptibility in (anti)ferromagnetic materials. These results present evidence in support of the theoretical model of interface pinning in random systems by Nattermann *et al.* and show that the same theoretical approach may be used for description of domain-wall pinning processes in all ferroic systems.

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