Comments and Addenda

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Hysteresis-Loop Measurements of Critical-Point Exponents in Ferroelectrics

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Some comments are made on a recent letter by J. A. Gonzalo emphasizing the importance of the electrocaloric effect in hysteresis-loop measurements close to a critical point.

In a recent letter, Gonzalo[1] reported a set of critical exponents for the ferroelectric triglycine sulphate (TGS) obtained on the basis of hysteresis-loop measurements. It is the purpose of this comment to point out that, even if it is assumed as it was in Ref. 1 that domain-wall motion plays a negligible role on the measurements reported, a correction should be made to the published data to account for the electrocaloric effect which can make the agreement with molecular-field theory (MFT), at least close to the transition, less satisfactory than in the original report.

In a 60-Hz hysteresis-loop measurement, such as those reported by Gonzalo, the frequency is quite high compared with the reciprocal of any appropriate thermal relaxation time characterizing the coupling between the sample and temperature bath, so that the field application is essentially adiabatic. Changing the field from E_1 to E_2 will change the sample temperature by the electrocaloric effect. The temperature change will be given by

$$\Delta T=-\int_{E_1}^{E_2}\frac{T}{C_E}\left(\frac{\partial P}{\partial T}\right)_E dE\,, \tag{1}$$

where P is the polarization and C_E is the heat capacity at constant field. Equation (1) is easily obtained from the identity $(\partial T/\partial E)_S(\partial S/\partial T)_E(\partial E/\partial S)_T=-1$ and the Maxwell relation $(\partial S/\partial E)_T=(\partial P/\partial T)_E$. Since the sample temperature will not in general coincide with that of the temperature bath, corrections should be made to data obtained using the hysteresis-loop method to account for this effect. These corrections can be serious in the immediate vicinity of the critical temperature, which is the region of greatest interest in the determination of critical exponents, because $(\partial P/\partial T)_E$ can become very large near T_c.

[1] J. A. Gonzalo, Phys. Rev. Letters **21**, 749 (1968).

If the complete electric equation of state were known, the correction for the electrocaloric effect could easily be calculated from Eq. (1). For TGS there seems to be general agreement[1–4] for $t=T_c-T$ greater than about 0.1°C that, with the exception of the heat capacity,[5] which seems better described in terms of a logarithmic divergence,[6,7] the equation of state given by MFT is sufficient. For $t<0.1$°C the situation is much less clear, for while there is no evidence of a departure from MFT in the susceptibility,[2,3] the only determination of the temperature dependence of the polarization which has been made using a technique other than uncorrected hysteresis-loop measurements[4] may not be in agreement with MFT, while the recent work of Gonzalo,[1] which reported agreement with MFT, should be corrected for the electrocaloric effect. Because for $t<0.1$°C the equation of state does not seem certain, and because of the method used by Gonzalo to choose T_c,[8] it is not at present possible to correct the data reported in Ref. 1 in an unambiguous manner. However, it should be emphasized that it is possible to obtain an empirical correction by direct measurements of the electrocaloric effect.

The corrections to the data of Ref. 1 due to the electrocaloric effect can be estimated in several ways. Perhaps the best way is by using the electrocaloric data

[2] J. A. Gonzalo, Phys. Rev. **144**, 662 (1966).
[3] P. P. Craig, Phys. Letters **20**, 140 (1966).
[4] B. A. Strukov, Phys. Status Solidi **14**, K135 (1966).
[5] B. A. Strukov, Fiz. Tverd. Tela **6**, 2862 (1964) [English transl.: Soviet Phys.—Solid State **6**, 2278 (1965)].
[6] J. Grindley, Phys. Letters **18**, 239 (1965).
[7] A logarithmic heat capacity divergence for a ferroelectric is consistent with a slight extension of MFT as shown in A. P. Levanyuk, Fiz. Tverd. Tela **5**, 1776 (1963) [English transl.: Soviet Phys.—Solid State **5**, 1294 (1964)]; Izv. Akad. Nauk SSSR **29**, 879 (1965).
[8] According to J. A. Gonzalo (private communication), the critical temperature used in Ref. 1 was chosen by taking as T_c the intercept of a plot of P^2 against T. This method of choosing T_c greatly complicates any correction of the data of Ref. 1 to include the electrocaloric effect.

of Strukov,[4] which are presented in terms of temperature change as a function of change in P^2, in conjunction with the data on the field dependence of P given in Fig. 1(a) of Ref. 1. For the point in Ref. 1 closest to T_c, reported at $t=0.042$°C, this calculation gives the temperature excursion of the sample as 0.019°C, quite comparable with the reported value of t. A second estimate can be made using Gonzalo's data which were fitted to $(\partial P/\partial T)_E = BE^{-1/3}$. Since C_E is less than the heat capacity in zero field C_0,[9] we will underestimate the temperature excursion by replacing C_E with C_0. If it assumed that the fractional temperature change is sufficiently small that T/C_0 is essentially constant, then Eq. (1) can be integrated to give $\Delta T = 3E_{\max}^{2/3}TB/2C_0$, which, when the numbers appropriate to the point at $t=0.042$°C are inserted, leads to an excursion of 0.008°C. Finally, if one neglects the field dependence of $(\partial P/\partial T)_E$ as well as of T/C_E, one finds the temperature excursion at the same point to be 0.02°C, if one uses Gonzalo's result for $(\partial P/\partial T)_0$ in the form $A/2t^{1/2}$. Since the first and third estimates are closer than are the first and second, one may suspect that the field dependence of $(\partial P/\partial T)_E$ at $t=0.042$°C is less rapid than $E^{-1/3}$. As an indication of the change in the critical exponents which such corrections can make, using the third estimate, which undoubtedly overestimates the correction, the exponent describing the temperature dependence of P is changed by 20%. The first estimate would yield a slightly smaller change than above, while the second would produce little change from the reported value.

As shown above, neglect of the electrocaloric effect can result in large relative uncertainties in t in the region of greatest interest when hysteresis-loop measurements are used to determine critical-point exponents. Thus it seems important that allowance for this effect be made in any future work using this technique for the determination of critical-point exponents or in assessing the uncertainties of any exponents determined using this technique without correction.

[9] B. A. Strukov, S. A. Taraskin, T. L. Skomorokohova, and K. A. Minaeva, Izv. Akad. Nauk SSSR **29**, 982 (1965).