Equation of State for the Cooperative Transition of Triglycine Sulfate near T_c

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(Received 13 June 1969)

Measurements of polarization versus field in the vicinity of the Curie temperature from triglycine sulfate, both *below* and *above* T_c, allow first, the determination of a number of critical exponents and second, the characterization of the ferroelectric equation of state. The relationship, below and above T_c, between the "scaled" variables $\hat{P}/[1-(T/T_c)]^\beta$ and $\hat{E}/[1-(T/T_c)]^{\beta\delta}$ was determined from a log-log plot which showed clearly a well-defined asymptotic behavior for the small and large "scaled" field. Comparison of the scaled data with the results from the mean-field theory showed good agreement. A phenomenological expression for the equation of state which matches all the empirical and homogeneity requirements has been formulated. Evidence for the validity of this equation of state for other transitions for which accurate data are available is discussed.

INTRODUCTION

THE second-order transition in ferroelectric triglycine sulfate (TGS) seems to be a very good test case for the mean-field theory. Previous work[1,2] has shown that the behavior of the dielectric constant and the spontaneous polarization is in agreement with the mean-field predictions. The present investigation, partially reported in a previous letter,[3] aimed at a more complete analysis of the order-disorder cooperative transition by means of a detailed study of the variation of polarization with electrical field as well as with temperature near the critical point. Accurate data of P versus E near T_c allow the determination of critical exponents through log-log graphic representations. In addition, once the two fundamental parameters β and δ, defined by $(P_s)_{T\sim T_c}=\text{const}\times[1-(T/T_c)]^\beta$ and $(P)_{T\sim T_c}=\text{const}\times E^{1/\delta}$, are determined, the way is open for the search of a "law of corresponding states" in terms of the properly "scaled" variables.

EXPERIMENTAL

The sample preparation and experimental procedure were described[1,3] in previous communications. The determination of the Curie temperature was done in two different ways. First, a plot of the squared spontaneous polarization (P_s^2) versus temperature was made which showed an almost perfect linear behavior yielding T_c by extrapolation to $P_s^2=0$. Alternatively, the method described by Kouvel and Fisher[4] was used, yielding the same result within experimental accuracy. It has been noted by Reese[5] that corrections due to the

* Operated by the University of Puerto Rico for the U. S. Atomic Energy Commission.

[1] J. A. Gonzalo, Phys. Rev. **144**, 662 (1966).
[2] P. P. Craig, Phys. Letters **20**, 140 (1966).
[3] J. A. Gonzalo, Phys. Rev. Letters **21**, 749 (1968).
[4] J. S. Kouvel and M. E. Fisher, Phys. Rev. **136**, A1626 (1964).
[5] W. Reese (private communication). It should be noted that precisely because of the method we have used to determine T_c, in spite of the fact that the corrections due to the electrocaloric effect can affect the absolute value of T, the associate correction in (T_c-T) should go to *zero* as one approaches T_c, the temperature at which the hysteresis loops are recorded to practically disappear. Recently, very accurate experiments by E. Nakamura *et al.*, [Proceedings of the Second International Meeting on Ferroelectricity, Kyoto, Japan, 1969 (unpublished)] free from electrocaloric effects, establish conclusively the classical values pre-

electrocaloric effect should be considered. While the accurate determination of these corrections near T_c is not easy, reasonable estimates indicate that our results would not be substantially altered by them. It may also be noted that perfect compensation of the P-versus-E hysteresis loops very near T_c could not be fully achieved with the Sawyer-Tower circuit, possibly due to a field dependence of the conductivity of the crystal. This behavior actually set limits of $\Delta T = T_c - T$ at $+0.02$ and $-0.04°C$ within which a reliable determination of P for very small E was not possible.

As is well known, an increase of the amplitude of the ac field applied to the sample for displaying the P-versus-E curve, produces a relatively small increase of the absolute value of the polarization with respect to the corresponding values for lower ac amplitude. However, the relative variation of the polarization as a function of temperature was checked for various field amplitudes and it was found to be the same, the absolute values being different only by a constant factor. This effect might be attributed to a consistently partial switching of the ferroelectric domains at low ac amplitudes. The constant ac field amplitude chosen in our case, $E=190$ V/cm, was relatively low, which helps to keep down the electrocaloric effect in the vicinity of T_c.

RESULTS

The experimental results below T_c as described in a previous letter,[3] were shown to yield the value of the critical exponents δ and β, along with four other exponents indicating the field and temperature dependence of both derivatives of the polarization with respect to field and temperature. The experimental values obtained from log-log plots of the data are given in Table I and compared with those calculated from the mean-field model, using the expression[6]

$$\hat{E} = (1-t)\tanh^{-1}(\hat{P}) - \hat{P},$$

$$[\hat{E}=E/E_0,\ t=1-(T/T_c),\ P=P/N\mu]$$

viously reported for the exponents γ and β, the former even at temperatures as close to T_c as $T_c-T\sim0.01°C$.

[6] J. A. Gonzalo and J. R. López-Alonso, J. Phys. Chem. Solids **25**, 303 (1964).

TABLE I. Experimental critical exponents from TGS compared with mean-field theory predictions.

Defining relationship	Experimental value	Mean-field relationship	Theoretical value
$(P)_{t=0} \sim e^{\gamma_3}$	$\gamma_3 = \dfrac{1}{\delta} = 0.32 \pm 0.02$	$(p)_{t=0} = (3e)^{1/3}$	$\gamma_3 = \dfrac{1}{\delta} = \tfrac{1}{3}$
$(p)_{e=0} \sim t^{\gamma_4}$	$\gamma_4 = \beta = 0.50 \pm 0.03$	$(p)_{e=0} = (3t)^{1/2}$	$\gamma_4 = \beta = \tfrac{1}{2}$
$\left(\dfrac{\partial p}{\partial e}\right)_{t=0} \sim e^{\gamma_7}$	$\gamma_7 = -0.66 \pm 0.05$	$\left(\dfrac{\partial p}{\partial e}\right)_{t=0} = \dfrac{(1-p^2)}{p^2}$	$\gamma_7 = -\tfrac{2}{3}$
$\left(\dfrac{\partial p}{\partial e}\right)_{e=0} \sim t^{\gamma_8}$	$\gamma_8 = -\gamma' = -0.95 \pm 0.10$	$\left(\dfrac{\partial p}{\partial e}\right)_{e=0} = \dfrac{(1-p^2)}{(t-p^2)}$	$\gamma_8 = -1$
$\left(\dfrac{\partial p}{\partial t}\right)_{t=0} \sim e^{\gamma_9}$	$\gamma_9 = -0.33 \pm 0.05$	$\left(\dfrac{\partial p}{\partial t}\right)_{t=0} = \dfrac{\tanh^{-1} p (1-p^2)}{p^2}$	$\gamma_9 = -\tfrac{1}{3}$
$\left(\dfrac{\partial p}{\partial t}\right)_{e=0} \sim t^{\gamma_{10}}$	$\gamma_{10} = -0.45 \pm 0.10$	$\left(\dfrac{\partial p}{\partial t}\right)_{e=0} = \dfrac{-\tanh^{-1} p (1-p^2)}{(t-p^2)}$	$\gamma_{10} = -\tfrac{1}{2}$

where $E_0 \simeq 4.4 \times 10^6$ V/cm is the saturation internal field, and $N\mu \simeq 4.3$ μC/cm^2 is the saturation polarization. It is interesting to note that, as it should be expected (see Appendix), the ratio of the two critical exponents relating the same derivative of the free energy to field and temperature is constant.

In Table II a summary of data for polarization and field at various temperatures *below* and *above* T_c is given. These data were "scaled" to determine $p = \hat{P}/t^\beta$ and $e = \hat{E}/t^{\beta\delta}$, and plotted using a log-log scale. It can be seen from Fig. 1 that the scaling of the data is quite good, giving evidence of the existence of a law of corresponding states. From this, the sequence of critical exponents, found directly and reported in the

previous short communication,[3] results in an automatic fashion. What is more important, however, is the fact that this log-log representation, which shows the critical behavior over a wide range of three decades in the reduced field e, shows clearly the asymptotic behavior of the equation of state for both small and large e, above and below T_c. This asymptotic character is in complete analogy with the observations of Green et al.[7] for liquid-vapor transitions in a good number of systems. We have also recently examined very accurate data[8,9] from ferromagnetic transitions, and the asymptotic trend for small and large scaled magnetic field is seen again to be fully analogous.

The asymptotic behavior can be summarized as

TABLE II. Polarization versus field for TGS from hysteresis loops in the vicinity of the Curie temperature, $T_c \simeq 322.50$°K.

	Below Curie temperature			Above Curie temperature	
$P(\mu C/cm^2)$	$\Delta T(\times 10^{-2}$ °C$)$	$E(V/cm)$	$P(\mu C/cm^2)$	$\Delta T(\times 10^{-2}$ °C$)$	$E(V/cm)$
0.217	4.2	49.7	0.1085	2.3	12.7
0.217	10.7	27.7	0.1085	8.7	21.1
0.217	17.1	9.3	0.1085	15.2	30.3
0.244	4.2	73.0	0.1085	21.7	40.2
0.244	10.7	46.9	0.163	2.3	33.1
0.244	17.1	24.5	0.163	8.7	49.3
0.271	4.2	101.8	0.163	15.2	60.6
0.271	10.7	72.4	0.163	21.7	71.9
0.271	17.1	46.4	0.217	2.3	69.8
0.271	30.1	7.0	0.217	8.7	88.1
0.298	4.2	137.9	0.217	15.2	104.3
0.298	10.7	104.5	0.217	21.7	117.7
0.298	17.1	74.6	0.298	2.3	131.8
0.298	30.1	25.4	0.298	8.7	148.7
0.326	4.2	182.7	0.298	15.2	166.4
0.326	10.7	144.5	0.298	21.7	186.1
0.326	17.1	104.6			
0.326	30.1	53.8			
0.326	43.0	9.9			

[7] M. S. Green, M. Vicentini-Missoni, and J. M. H. Levelt Sengers, Phys. Rev. Letters **18**, 1113 (1967).
[8] J. S. Kouvel and J. B. Comly, Phys. Rev. Letters **20**, 1237 (1968).
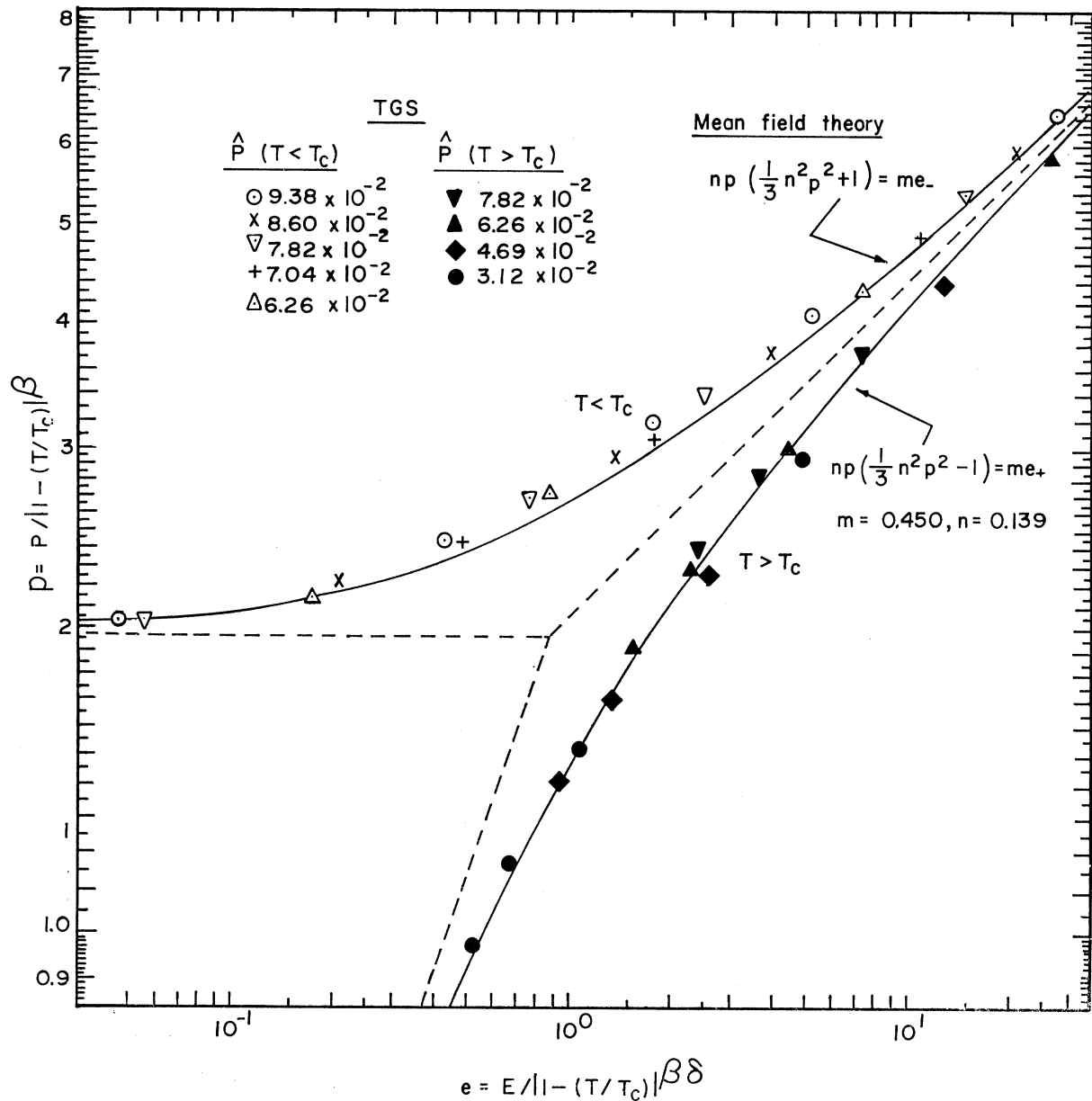[9] J. T. Ho and J. D. Litster, Phys. Rev. Letters **22**, 603 (1969).

FIG. 1. Log-log plot of the scaled polarization versus scaled electric field for ferroelectric TGS near the Curie temperature. Full line is renormalized mean-field equation of state with $m=0.450$, $n=0.139$.

follows:

$$\text{Below } T_c: \quad p \underset{e\to0}{\sim} \text{const}, \tag{1a}$$

$$p \underset{e\to\infty}{\sim} \text{const} \times e^{1/\delta}, \tag{1b}$$

$$\text{Above } T_c: \quad p \underset{e\to0}{\sim} \text{const} \times e \tag{2a}$$

$$p \underset{e\to\infty}{\sim} \text{const} \times e^{1/\delta}. \tag{2b}$$

The implications of these expressions are obvious: (1a) means that for $\hat{E} \ll t^{\beta\delta}$, below T_c, we are approach-

ing the coexistence curve, i.e., $P_s = \text{const} \times t^\beta$; (1b) and (2b) mean that for $\hat{E} \gg t^{\beta\delta}$ we are approaching the critical isotherm, i.e., $P = \text{const} \times E^{1/\delta}$; finally, (2a) means that for $\hat{E} \ll t^{\beta\delta}$, above T_c, we are approaching $\Delta P/\Delta E = \text{const} \times t^{-\gamma}$, with $-\gamma = \beta - \beta\delta = -\gamma'$ which in our case merely expresses the Curie-Weiss law.

MEAN-FIELD MODEL EQUATION OF STATE

The basic expression of the mean-field model for ferroelectrics can be written as

$$\hat{E}_\mp = (1 \mp t) \tanh^{-1}(\hat{P}) - \hat{P},$$

where $t=|1-(T/T_c)|$; the negative sign applies at $T<T_c$ and the positive sign at $T>T_c$. This equation can be expanded in the following way:

$$\hat{E}_{\mp}=(\hat{P}+\tfrac{1}{3}\hat{P}^3+\tfrac{1}{5}\hat{P}^5\cdots)\mp t(\hat{P}+\tfrac{1}{3}\hat{P}^3+\tfrac{1}{5}\hat{P}^5\cdots)-\hat{P}$$
$$=\mp t\hat{P}+\tfrac{1}{3}\hat{P}^3+(\tfrac{1}{5}\hat{P}^5+\cdots)\mp t(\tfrac{1}{3}\hat{P}^3+\tfrac{1}{5}\hat{P}^5\cdots).$$

Putting $e\equiv\hat{E}/t^{3/2}$ and $p=\hat{P}/t^{1/2}$,

$$e_{\mp}=\mp p+\tfrac{1}{3}p^3+t[\mp\tfrac{1}{3}p^3+\tfrac{1}{5}p^5(1\mp t)+\cdots].$$

Obviously, if $t\ll1$ (for instance, $1.0\times10^{-5}\leqslant t\leqslant3.0\times10^{-3}$ in our experiment) this expression reduces itself to

$$e_-=p(\tfrac{1}{3}p^2-1)\quad\text{for}\quad T<T_c,\qquad(3a)$$
$$e_+=p(\tfrac{1}{3}p^2+1)\quad\text{for}\quad T>T_c.\qquad(3b)$$

To check these equations against the experimental results it has been found necessary to introduce proportionality factors for e and p in the above equations. They became

$$me_-=np(\tfrac{1}{3}n^2p^2-1),$$
$$me_+=np(\tfrac{1}{3}n^2p^2+1).$$

To introduce these proportionality factors is equivalent to modifying the normalization parameters in such a way that $(N\mu)/n$ replaces $(N\mu)$, and E_0/m replaces E_0. The best fit to the data is obtained with

$$m=0.450,\quad n=0.139.$$

Figure 1 shows a plot of the mean-field equation of state in scaling form, along with the experimental data. The agreement is very good except for a few points for $T<T_c$ in the intervening region between small and large e, which fall slightly above the theoretical curve. The estimated experimental errors go from 5 to 1% as p increases and from 10 to 2% as e increases.

PHENOMENOLOGICAL EQUATION OF STATE

The realization that the asymptotic behavior specified by Eqs. (1a)-(2b) is not only characteristic of our ferroelectric cooperative transition, but also of liquid-vapor and magnetic cooperative transitions, strongly suggests the convenience of using it along with Widom's homogeneity requirements to specify the equation of state for the system under consideration throughout T_c and in its vicinity.

Since the formulation of the homogeneity assumption[10] for the free energy of a cooperative system undergoing a second-order phase transition, considerable progress has been made in the understanding of the critical phenomena.[11] Griffiths[12] has studied the problem of constructing explicit analytic expressions for the equation of state relating the scaled extensive variable (polarization, magnetization, volume, etc.) to the intensive variable (electric field, magnetic field, pressure, etc., respectively) for the case of rational critical

exponents. Very recently, several empirical[9,13] and parametric[14] expressions have been proposed to fit the equation of state of some real systems. We wish to construct a compact expression of the free energy in a simple way, matching the critical exponents sequence both above T_c and below it, as well as the asymptotic behavior indicated in the preceding paragraph, from the law of corresponding states.

Let us assume, following Widom[10] and Griffiths,[12] that the free energy about the critical point can be given simultaneously by

$$F(\hat{X},t)=\hat{X}^{(\delta+1)/\delta}\left[a_1+a_2\left(\frac{t}{\hat{X}^{1/\beta\delta}}\right)+a_3\left(\frac{t}{\hat{X}^{1/\beta\delta}}\right)^2+\cdots\right]$$
$$\text{for }\hat{X}^{1/\beta\delta}\gg t\quad(T\lesseqgtr T_c)\quad(4a)$$

$$F(\hat{X},t)=t^{\beta(\delta+1)}\left[b_1+b_2\left(\frac{\hat{X}}{t^{\beta\delta}}\right)+b_3\left(\frac{\hat{X}}{t^{\beta\delta}}\right)^2+\cdots\right]$$
$$\text{for }t^{\beta\delta}\gg\hat{X}\quad(T<T_c).\quad(4b)$$

Here $\hat{X}=X/X_0$ is the reduced intensive variable, and $t=1-(T/T_c)$ the reduced temperature. [It may be noted that while the expansion (4b) is very familiar in the literature since the introduction of the homogeneity assumption, relatively less attention has been paid to the complementary expansion (4a); Ho and Litster have made use of the latter in their recent work[9] on CrBr$_3$.]

These expansions ensure a sequence of critical exponents of the expected form

$$(F)_{t=0}\sim\hat{X}^{(\delta+1)/\delta},\quad S=(\partial F/\partial t)_{t=0}\sim\hat{X}^{(\delta+1)/\delta-(1/\beta\delta)},$$
$$C=(\partial^2F/\partial t^2)_{t=0}\sim\hat{X}^{(\delta+1)/\delta-2(1/\beta\delta)}\cdots,\quad(5a)$$

$$(F)_{x=0}\sim t^{\beta(\delta+1)},\quad\hat{Y}=(\partial F/\partial\hat{X})_{x=0}\sim t^{\beta(\delta+1)-\beta\delta},$$
$$\hat{Y}_x{}'=(\partial^2F/\partial\hat{X}^2)_{x=0}\sim t^{\beta(\delta+1)-2\beta\delta}\cdots,\quad(5b)$$

where the "gap" exponents are $(1/\Delta)=1/\beta\delta$ and $\Delta=\beta\delta$, respectively.

The last two expressions of (5b) are easily recognizable as the defining equations for the indices β and $-\gamma=\beta-\Delta$, respectively. Let us call $\hat{Y}$ the partial derivative of the free energy with respect to the variable $\hat{X}$. Its meaning will be, of course, that of the respective extensive variable in the various cases (polarization, magnetization, volume, etc.). From (4a) we obtain

$$\hat{Y}=\frac{\partial F}{\partial\hat{X}}=\hat{X}^{1/\delta}\left[a_1+a_2\left(\frac{t}{\hat{X}^{1/\beta\delta}}\right)+a_3\left(\frac{t}{\hat{X}^{1/\beta\delta}}\right)^2+\cdots\right]$$
$$+\hat{X}^{1/\delta}\left[a_2+2a_3\left(\frac{t}{\hat{X}^{1/\beta\delta}}\right)+3a_3\left(\frac{t}{\hat{X}^{1/\beta\delta}}\right)^2+\cdots\right]$$
$$\times\left(-\frac{1}{\beta\delta}\right)\left(\frac{t}{\hat{X}^{1/\beta\delta}}\right),\quad(6a)$$

[10] B. Widom, J. Chem. Phys. **43**, 3898 (1965).
[11] See, for example, M. E. Fisher, Rept. Progr. Phys. **30**, 615 (1967).
[12] R. B. Griffiths, Phys. Rev. **158**, 176 (1967).

[13] M. Vicentini-Missoni, J. M. H. Levelt Sengers, and M. S. Green, Phys. Rev. Letters **22**, 389 (1969).
[14] P. Schofield, Phys. Rev. Letters **22**, 606 (1969).

$$\hat{Y} = \frac{\partial F}{\partial \hat{X}} = t^\beta \left[b_2 + 2b_3 \left(\frac{\hat{X}}{t^{\beta\delta}}\right) + 3b_4 \left(\frac{\hat{X}}{t^{\beta\delta}}\right)^2 + \cdots \right], \quad (6b)$$

or in other words

$$y = \hat{Y}/t^\beta = x^{1/\delta} [c_1 + c_2(x^{-1/\beta\delta}) + c_3(x^{-1/\beta\delta})^2 + \cdots]$$
$$\text{for } x \equiv \hat{X}/t^{\beta\delta} \gg 1 \quad (T \lesseqgtr T_c) \quad (7)$$

$$y = [d_1 + d_2(x) + d_3(x)^2 + \cdots] \text{ for } x \ll 1 \quad (T < T_c). \quad (8)$$

Our aim is to get a single expression for y which combines Eqs. (7) and (8) at $T < T_c$, approaching each of them for the limiting cases of $x \gg 1$ and $x \ll 1$. One can write formally

$$y = x^{1/\delta}\psi_1(x^{-1/\beta\delta}) + \psi_2(x) \quad \text{for} \quad T < T_c, \quad (9)$$

$$y = x^{1/\delta}\psi_1(x^{-1/\beta\delta}) \quad \quad \text{for} \quad T < T_c, \quad (10)$$

where ψ_1 and ψ_2 stand for the factors within brackets in Eqs. (7) and (8). This is our equation of state which already involves the correct sequence of critical exponents throughout the series expansion of ψ_1 in powers of $x^{-1/\beta\delta}$ and of ψ_2 in powers of x. Below T_c, according to Eqs. (4a) and (4b), $\psi_1(x^{-1/\beta\delta})$ should predominate for $x \gg 1$, and $\psi_2(x)$ for $x \ll 1$. Above T_c, it is clear that the spontaneous order ceases to be nonzero for $x = 0$, so it is reasonable to eliminate the contribution from $\psi_2(x)$. At this point, the empirical asymptotic behavior indicated in the preceding paragraph should be incorporated. Below T_c, for $x \ll 1$, $\psi_2(x)$ should approach a constant, and for $x \gg 1$, $\psi_1(x^{-1/\beta\delta})$ should also approach a constant, according to (1a) and (1b), respectively. Above T_c, $\psi_2(x)$ does not exist and $\psi_1(x^{-1/\beta\delta})$ should approach a value proportional to $x^{1-(1/\delta)}$ for $x \ll 1$, remaining the same as below T_c for $x \gg 1$. One could try different functional expressions for ψ_2 and ψ_1, all of them susceptible to being expanded in the power series of the required form. In principle, a logarithm, a binomial, or an exponential would meet this requirement. However, after testing these three forms against the experimental data, not only for TGS but for magnetic and liquid-vapor systems, one comes to the conclusion that the logarithm changes too slowly with x and the exponential, on the other hand, too rapidly, in order to satisfy the asymptotic behavior indicated. On this ground, only the binomial form is left as a satisfactory one. The simplest binomial forms one can think of, meeting the above mentioned requirements, are

$$\psi_1(x^{-1/\beta\delta}) = A\left[1 + \left(\frac{x}{x_1}\right)^{-1/\beta\delta}\right]^{-\beta\delta(1-1/\delta)}, \quad (11a)$$

$$\psi_2(x) = B\left[1 + \left(\frac{x}{x_2}\right)\right]^{-(1/\beta\delta)(1-\beta)}. \quad (11b)$$

The exponents $-\beta\delta(1-1/\delta)$ in Eq. (11a), and $-(1/\beta\delta)(1-\beta)$ in Eq. (11b), are the simplest ones which keep the homogeneity of Eq. (9) from $x/x_1 \ll 1$

to $x/x_2 \gg 1$ through the whole range in x. Also, the former is automatically required by the condition (2b).

As a check of the "phenomenological" equation of state obtained, the principal critical exponents may be calculated. Below T_c, from Eqs. (6)–(10), one obtains

$$x \ll x_1, \quad \hat{Y} \simeq \psi_2 t^\beta \simeq B t^\beta, \quad (12)$$

$$x \gg 1, \quad \hat{Y} \simeq \psi_1 \hat{X}^{1/\delta} \simeq A \hat{X}^{1/\delta}, \quad (13)$$

$$x \ll 1, \quad \partial \hat{Y}/\partial \hat{X} = \hat{X}^{1/\delta} \partial \psi_1/\partial \hat{X} + (1/\delta) X^{(1/\delta)-1}\psi_1$$
$$+ t^\beta \partial \psi_2/\partial \hat{X} = C_1 t^{\beta-\beta\delta} = C_1 t^{-\gamma'}. \quad (14)$$

Similarly, above T_c,

$$x \ll 1, \quad \hat{Y} \simeq \psi_1 \hat{X}^{1/\delta} \simeq 0, \quad (15)$$

$$x \gg 1, \quad \hat{X} \simeq \psi_1 \hat{X}^{1/\delta} \simeq A \hat{X}^{1/\delta}, \quad (16)$$

$$x \ll 1, \quad \partial \hat{Y}/\partial \hat{X} = \hat{X}^{1/\delta} \partial \psi_1/\partial X + (1/\delta)\hat{X}^{(1/\delta)-1}\psi_1$$
$$= C_2 t^{\beta-\beta\delta} = C_2 t^{-\gamma}. \quad (17)$$

The constants which appear in Eqs. (14) and (17) are, respectively,

$$C_1 = \frac{A}{x_1^{1-(1/\delta)}} - \frac{1-\beta}{\beta\delta} \frac{B}{x_2} \quad \text{and} \quad C_2 = \frac{A}{x_1^{1-(1/\delta)}}.$$

It is interesting to note that $\gamma = \gamma'$, also supported by available experimental evidence.

COMPARISON WITH EXPERIMENTAL RESULTS

Figure 2 shows that the use of Eqs. (11a) and (11b) in the equation of state given by (9) and (10), leads to excellent agreement with the experimental data for ferroelectric TGS, below T_c as well as above T_c; in this case, $y = p$ (scaled polarization) and $x = e$ (scaled electric field). Only four dimensionless numerical parameters have been used, their values being

$$A = 2.12, \quad x_1 = e_1 = 0.907,$$
$$B = 1.87, \quad x_2 = e_2 = 1.425. \quad (18)$$

For various liquid-vapor systems, it was earlier reported by Green et al.[7] that the data suggest a scaling law asymptotic behavior as that indicated by Eqs. (1)–(2). Using Green's et al. critical exponents, $\beta = 0.35$ and $\delta = 5.0$, one could try to fit Eqs. (9) and (10) to the data, given in the chemical potential-density representation, in order to determine A, x_1, B, and x_2. Since the scattering of the experimental points (collected from many authors on many different systems and temperature intervals) is fairly high, it does not seem to be justified. However, accurate data[15] for He[4] are available. By using the tabulated data of Roach,[15] one can calculate the fundamental critical exponents in the pressure-volume representation. Since the transition occurs at very low temperature, it is not surprising that the asymetry of the experimental data is considerable. It is convenient to bypass this difficulty
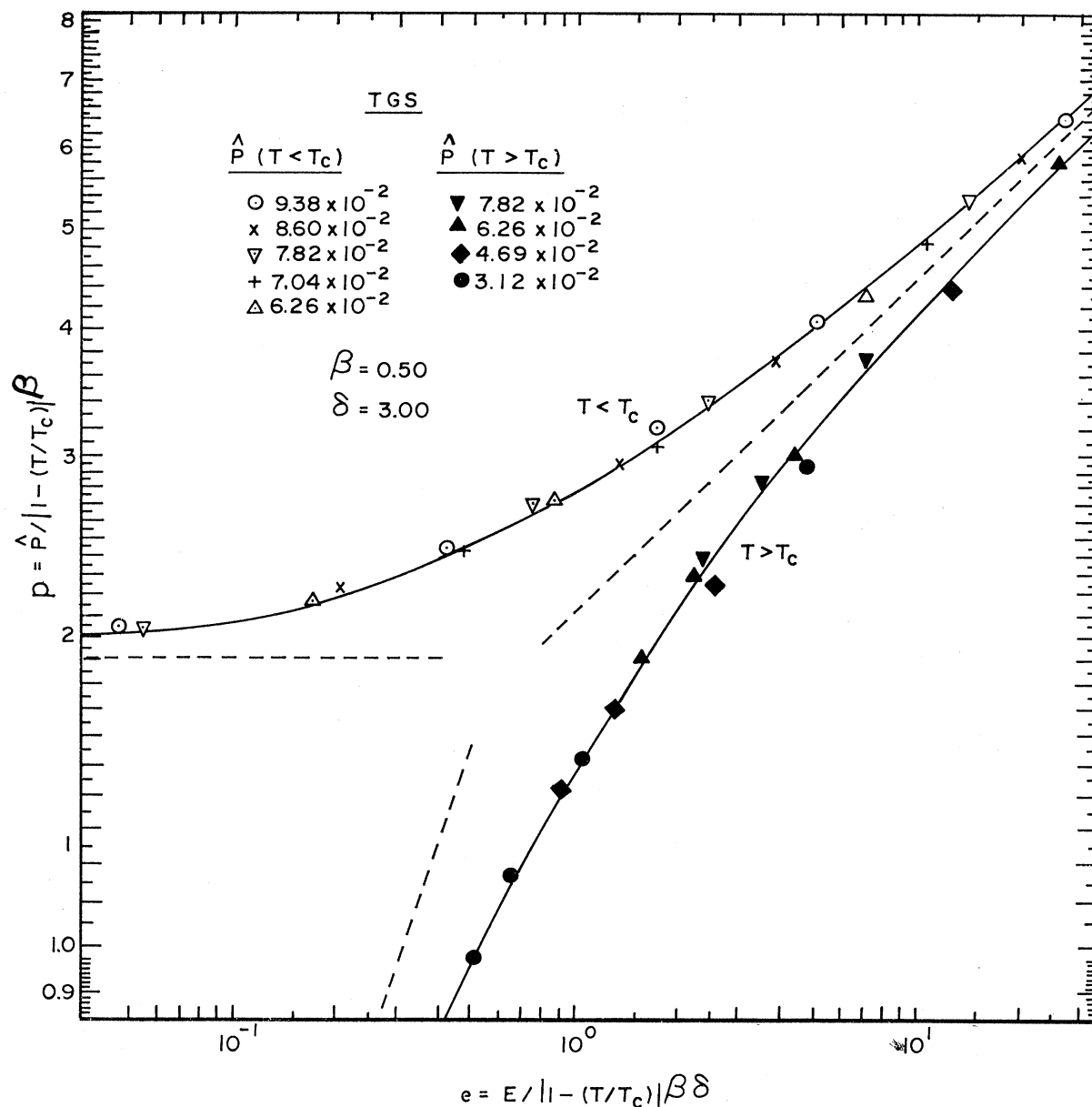
[15] P. R. Roach, Phys. Rev. 170, 213 (1968).

FIG. 2. Log-log plot of the scaled polarization versus scaled electric field for ferroelectric TGS near T_c. Full line is phenomenological equation of state with $A=2.12$, $B=1.87$, $x_1=0.907$, $x_2=1.425$.

by using the following definitions:

$$(V_{gas}-V_{liq}) \propto \Delta T^\beta \quad \text{(along coexistence curve)}, \quad (19)$$

$$V(-\Delta P)-V(+\Delta P) \propto \Delta P^{1/\delta}$$
$$\text{(along critical isotherm)}, \quad (20)$$

where V is volume, T is temperature, and P is pressure.

In this way, a nicely defined straight line for two decades up to the vicinity of the critical point, is obtained in the log-log plot, which yields β. The analog plot for δ is only approximately linear in the last decade up to the vicinity of the critical point and since the

trend suggests an increasing value of δ we extrapolate to the closest value which does not violate Griffith's inequality, taking $\alpha'\simeq0$. This results in

$$\beta=0.411 \quad \text{and} \quad \delta=3.84. \quad (21)$$

These numerical values are somewhat different from those obtained by Roach[15] and Vicentini-Missoni[13] but it should be taken into account that they used the density instead of the volume and neglected the asymmetry. By using the exponents given by Eq. (21) one can scale the data corresponding to several isotherms above and below T_c. The results are seen in Fig. 3(a)
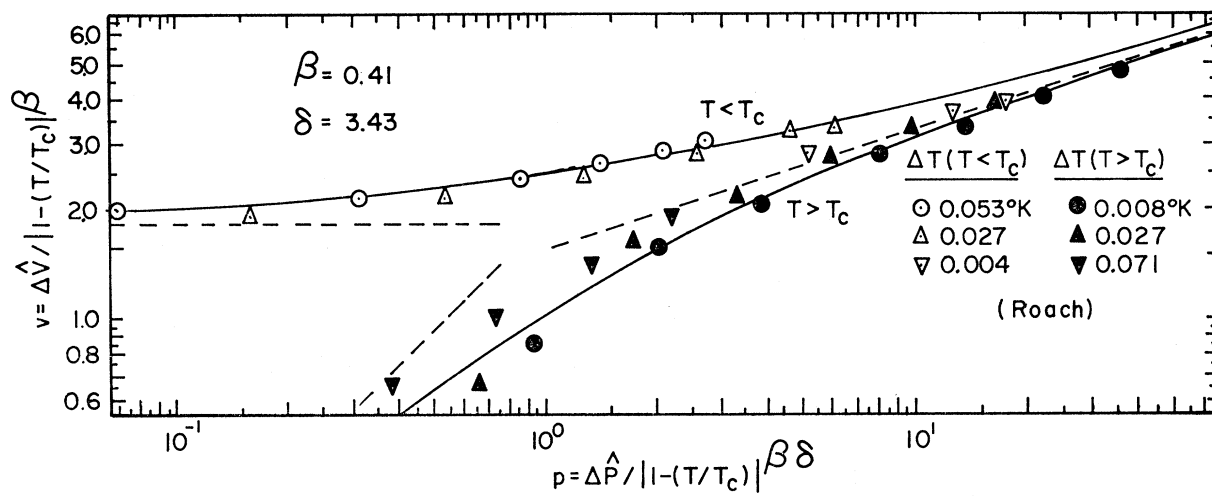
(a) Liquid—vapor He^4
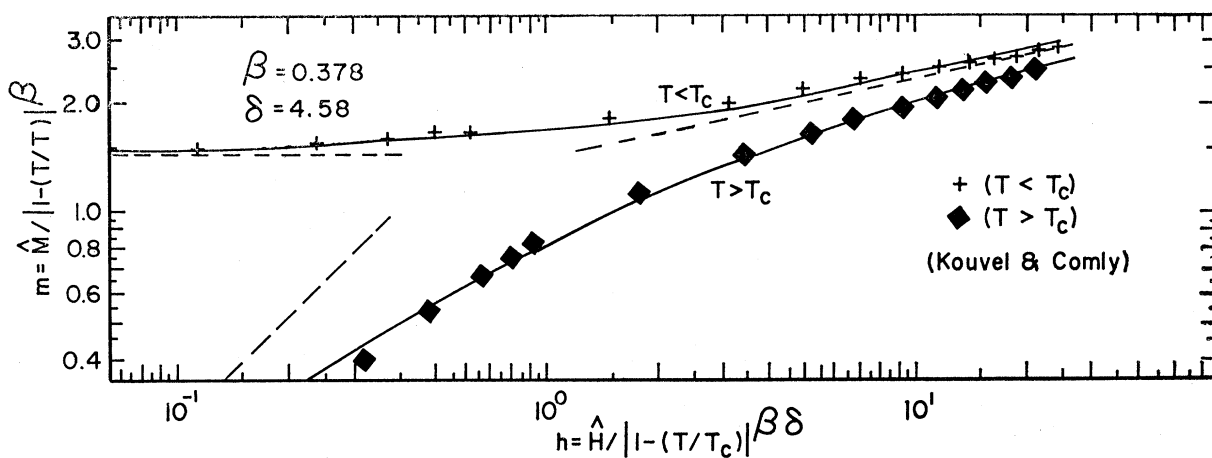
(b) Ferromagnetic Ni .

FIG. 3. Log-log plots of scaled quantities for (a) liquid-vapor He^4, volume versus pressure; (b) ferromagnetic Ni, magnetization versus magnetic field (averaged data). Full lines are phenomenological equations of state with (a) $A = 1.92$, $B = 1.83$, $x_1 = 7.57$, $x_2 = 11.3$; and (b) $A = 1.18$, $B = 1.42$, $x_1 = 0.334$, $x_2 = 0.360$.

where the phenomenological equation of state is represented, with

$$y = v = \frac{\Delta V/V_c}{t^\beta} \quad \text{and} \quad x = p = \frac{\Delta P/P_c}{t^{\beta\delta}},$$

where $V = 14.49$ cc (per gram), $T_c = 5.193°K$, $P_c = 1710.0$ Torr. The equation that best fits the data has been obtained by using the dimensionless parameters

$$A = 1.92, \quad x_1 = p_1 = 7.57, \tag{22}$$
$$B = 1.83, \quad x_2 = p_2 = 11.3.$$

An estimate of the experimental errors from Raach's data indicates that they go from 7 to 2% as v increases, and from 20 to 4% as p increases.

Finally, the accurate data for the ferroparamagnetic transition in Ni, by Kouvel and Comly,[8] have also been examined. The result is shown in Fig. 3(b). Again, the corresponding phenomenological equation of state is plotted with

$$y = m = \frac{M/M_0}{t^\beta} \quad \text{and} \quad x = h = \frac{H/H_0}{t^{\beta\delta}},$$

where $M_0 = 58.6$ emu/g, $H_0 = kT_c/\mu_0 = 15.2 \times 10^6$ Oe. The equation that best fits the data is obtained with

$$A = 1.183, \quad x_1 = h_1 = 0.334, \tag{23}$$
$$B = 1.421, \quad x_2 = h_2 = 0.360.$$

TABLE III. Comparison of critical exponents and coefficients (see text) for various real systems and the mean-field model.

System	β	δ	$\beta\delta$	A	B
Ferroelectric TGS	0.50	3.0	1.50	2.12	1.87
Liquid-vapor He[4]	0.41	3.8	1.57	1.92	1.83
Ferromagnetic Ni	0.38	4.6	1.74	1.18	1.42
Mean field	0.500	3.00	1.500	1.44	1.73

Since no tables are given in Ref. 8 we cannot give an estimate of the relative errors. However, they must be small, given the small scattering of points in the graphs.

In Table III, a comparison is made of the main critical exponents and coefficients for TGS, He[4] and Ni, along with those of the mean-field theory.

SUMMARY AND CONCLUSIONS

The principal conclusions of the present work may be stated briefly as follows:

(1) The scaled data for P versus E from TGS in the vicinity and at both sides of T_c satisfy very approximately the mean-field theory predictions.

(2) A phenomenological equation of state has been constructed, based on the homogeneity assumption, which is simpler than previous proposals and reflects in a natural way the different asymptotic behavior for low- and high-scaled intensive variable (electric field in the case of TGS).

(3) The application of this phenomenological equation of state to representative ferroelectric, liquid-vapor, and ferromagnetic transitions shows fair agreement with the data in all three cases.

In the case of TGS, the agreement is excellent and improves that of the mean-field theory. All experimental points are within the estimated error limits. In the case of He[4] there is appreciable scattering of points at low p above T_c, and at high p below T_c. However, taking into account the experimental uncertainties, the agreement is fair. In the case of Ni, for which very accurate data are available, the agreement is also fair, but some small systematic deviations seem to be present, especially for $T > T_c$.

ACKNOWLEDGMENTS

APPENDIX

From inspection of Eqs. (3a) and (3b), it is readily seen that the two critical exponents from the same derivative of the free energy, $F_{n,m} = \partial^{n+m} F / \hat{X}^n \partial t^m$, are related in a simple way. Let us call γ_k and γ_{k+1} to the exponents which define the dependence with $\hat{X}$ and t, respectively. They are

$$\gamma_k = (\delta+1)/\delta - m(1/\beta\delta) - n,$$
$$\gamma_{k+1} = \beta(\delta+1) - n\beta\delta - m, \tag{A1}$$

as obtained by using Eq. (4a) for γ_k and Eq. (4b) for γ_{k+1}. These exponents define the relationships

$$F_{m,n} \sim \hat{X}^{\gamma_k}, \quad (\hat{X} \gg t^{1/\beta\delta}),$$
$$F_{m,n} \sim t^{\gamma_{k+1}}, \quad (t^{\beta\delta} \gg \hat{X}). \tag{A2}$$

The ratio is then

$$\frac{\gamma_k}{\gamma_{k+1}} = \frac{(\delta+1)/\delta - m(1/\beta\delta) - n}{\beta\delta(\delta+1)/\delta - n\beta\delta - m} = \frac{1}{\beta\delta} = \text{const.} \tag{A3}$$

This general *equality* is quite useful, and is already implicit in earlier theoretical work (see Fisher's[12] work and references therein.) By using Eq. (A3), one can easily construct equalities relating triads of critical exponents. Let us take, for instance, the four most commonly used exponents, i.e., δ(critical isotherm), β(coexistence curve), $-\gamma'$ (compressibility versus temperature), and $-\alpha'$ (specific heat versus temperature). Four triads can be made in the following way:

$$[(1/\delta)+1]/(-\alpha'+2) = 1/\beta\delta,$$
$$\text{i.e., } \alpha' + \beta(1+\delta) = 2, \tag{A4}$$

$$[(1/\delta)-1]/(-\gamma') = 1/\beta\delta,$$
$$\text{i.e., } +\gamma' + \beta(1-\delta) = 0, \tag{A5}$$

and eliminating successively β and δ from Eqs. (A4) and (A5),

$$\alpha' + 2\delta - \gamma' - \delta(\alpha' + \gamma') = 2, \tag{A6}$$

$$\alpha' + \gamma' + 2\beta = 2. \tag{A7}$$

The expressions (A4), (A5), and (A7) can be recognized as the equality form of relationships introduced by Griffiths, Widom (also referred to as Kouvel-Rodbell relation), and Fisher-Rooshbrook. By using (A3), any desired relationship between three arbitrary critical exponents may be easily obtained.

The series of experimental exponents available from TGS enable a direct experimental check on the constancy of the exponent ratio specified by Eqs. (A3). Table I shows that the critical exponents associated with $F_{1,0} = P$, $F_{2,0} = \partial P/\partial E$, and $F_{1,1} = \partial P/\partial T$ satisfy the expected ratio $\gamma_k/\gamma_{k+1} = \frac{3}{2}$.