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The paraelectric susceptibility scaling function for the ferroelectrics triglycine sulphate and triglycine selenate

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Abstract. A form of the scaling function is proposed which gives a considerably more accurate description of the critical properties of the ferroelectrics triglycine sulphate and triglycine selenate in the paraelectric phase than the theoretical models hitherto applied, i.e. the Landau theory and the approximate model based on the Larkin–Khmelnitskii theory.

1. Introduction

Neither the Ginzburg–Landau–Wilson model of phase transition plus the renormalization group and ε-expansion, nor the series analysis by the Padé approximants method for the Ising and Heisenberg model explains the very small corrections to the classical values of critical indices. There is also available the theory of Larkin and Khmelnitskii (1969) theory for uniaxial ferroelectrics (Aharony 1973), in which the classical critical exponents are modified by logarithmic corrections. From this theory is derived the equation of state (Bervillier 1975, Binder *et al* 1976)

$$E = a(\tau\tilde{P} + \tfrac{1}{6}g\tilde{P}^3) \qquad \tilde{P} = dP|\ln(\tau + 0.5ga^2P^2|^{-1/3} \tag{1}$$

where a, d and g are phenomenological constants, E is the electric field, P is the polarization, and $\tau = T/T_c - 1$ is the reduced temperature. This equation may be expanded in a series. In the paper by Binder *et al* (1976) this is given up to the order of P^5. The equivalent equation of state but to the power P^3, also taking into account the crossover molecular field theory (MFT) Ising dipolar system, is derived from the free energy (Natterman 1978) for $T > T_c$:

$$F = \tfrac{1}{2}\alpha_0\tau q(\tau)P^2 + \tfrac{1}{4}\beta_0 q^3(\tau)P^4 \tag{2}$$

where $q(\tau) = [1 - 3b\ln(\tau/\tau_0)]^{-1/3}$ and α_0, β_0, γ_0, τ_0 and b (>0) are parameters.

From analysis of high-temperature series expansions by means of the Padé approximants it is known (Baker and Gaunt 1967, Fisher 1967) that it is very difficult to distinguish between the logarithmic singularities and small critical exponent singularities ($\tau^{-\alpha} \simeq 1 - \alpha\ln\tau$, $|\alpha| \ll 1$). Additionally, the previously conducted analysis of experimental data for ferroelectrics exhibiting 'quasi-Landau' critical behaviour (Fugiel 1989) indicates that the difference between a small critical exponent correction and a logarithmic correction lies within the limits of experimental error. In the case of the free-energy equation (2) this indistinguishability signifies satisfying the condition

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$3b|\ln(\tau/\tau_0)| \ll 1$. Therefore we can use the approximation $\exp[-3b\ln(\tau/\tau_0)] = 1 - 3b\ln(\tau/\tau_0)$. Then the logarithmic correction $q(\tau)$ in (2) may be interpreted in the sense of a small exponent $b > 0$:

$$q(\tau) = (\tau/\tau_0)^b \tag{3}$$

and equation (2) may be written as follows:

$$F = \tfrac{1}{2}C_2\tau^\gamma P^2 + \tfrac{1}{4}C_4\tau^{3b}P^4 \tag{4}$$

where $C_2 = \alpha_0/\tau_0^b$, $\gamma = 1 + b$ and $C_4 = \beta_0/\tau_0^{3b}$.

The model based on the energy equation (4) satisfactorily explains the slight deviations from the Landau critical exponents (Fugiel *et al* 1990). However, its deficiency is clearly observable when the susceptibility scaling function derived from (4) is compared with the corresponding experimental data. In accordance with (4), for the non-ordered phase this function may be written in the form

$$G(\chi_0/\chi) = 27\beta_0\alpha_0^{-3b/\gamma}\tau_0^{3b(b/\gamma-1)}E^2\chi_0^{2h} \tag{5}$$

where $G(x) = x^3 + 3x^2 - 4$, $\gamma = 1 + b$, $h = \Delta/\gamma = \delta/(\delta - 1)$, $\Delta = \frac{3}{2}$ and $\delta \neq 3$, are critical exponents and the reduced temperature is contained implicitly in the zero-field susceptibility ($\chi_0^{-1} = C_2\tau^\gamma$). Then, in accordance with (5), $G(\chi_0/\chi)$ is a linear function of the argument $E^2\chi_0^{2h}$. However, from the experimental results we have obtained for the ferroelectrics triglycine selenate (TGSe) and triglycine sulphate (TGS), it must be concluded that the relation $G(\chi_0/\chi)$ versus $E^2\chi_0^{2h}$, although it has the nature of a scaling function, is clearly non-linear, particularly for TGSe (figure 1). Therefore, to achieve better agreement with experiment, it becomes necessary to modify equation (5).

2. Results

The experimentally recorded non-linearity of the function $G(\chi_0/\chi)$ versus $E^2\chi_0^{2h}$ (figure 1 and figure 2) may, in the first approximation, be expressed as follows:

$$G(\chi_0/\chi) = a_1 y + a_2 y^2 \tag{6}$$

where $y = E^2\chi_0^{2h}$. On the basis of our experimental results we have, for both TGS and TGSe, $a_1 > 0$ and $a_2 > 0$. The satisfactory concentration of experimental points along the curve describing the polynomial (6) in figure 1 and figure 2 gives evidence of the fact that the approximation presented here is correct, or at least considerably better than function (5).

The physical arguments behind equation (6) are of the same type as given in the paper by Fugiel *et al* (1990) where it was shown that the function $G(\chi_0/\chi)^{1/2} = (\chi_0/\chi + 2)(\chi_0/\chi - 1)^{1/2}$ is non-linear in the argument $E\chi_0^h$ for TGS and TGSe crystals. This non-linearity is evidence that the higher-order terms $P^6, P^8, \ldots$ of free energy must give contributions to the scaling of the same order as those coming from P^2 and P^4 terms and this is in contradiction to the molecular-field theory in which $P^6, P^8, \ldots$ powers are insignificant in the neighbourhood of the critical point. The possibility that the higher-order powers P^{2n} ($n \geq 3$) may contribute to the scaling follows from the results reported by Domb and Hunter (1965) and by Patashinskii and Pokrovskii (1966), deduced on the basis of series analysis (plus extrapolation by Padé approximants) of high-temperature series expansions for the Ising model. Using this idea we derived equation (6) in a

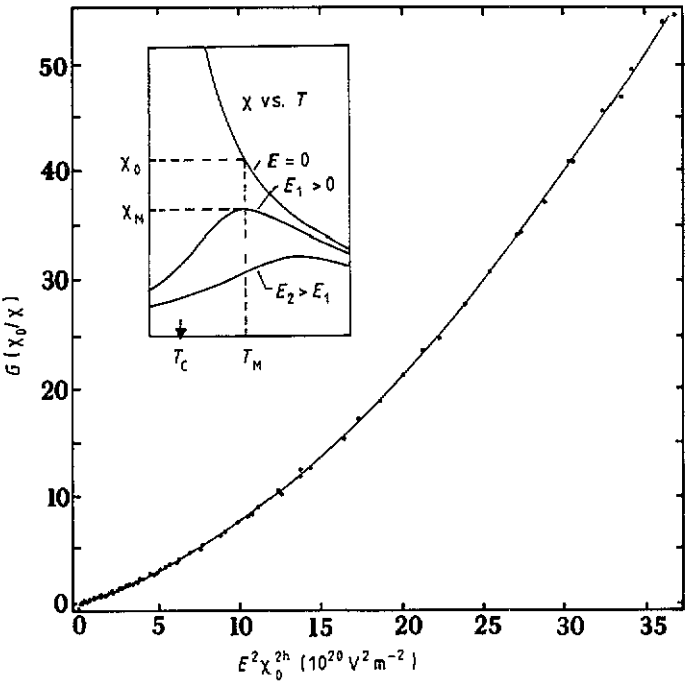

Figure 1. $G(\chi_0/\chi)$ versus $E^2\chi_0^{2h}$, where $h = \delta/(\delta - 1) = 1.45$ and $\delta = 29/9$ for TGSe. Values of χ_0 were determined at six temperatures in the interval corresponding to $10^{-3} < (T - T_c)/T_c < 10^{-2}$ at atmospheric pressure. The susceptibility χ was determined for each of six temperatures for about 15 values of field E. The full curve is the numerical fit according to equation (6) for $a_1 = 0.498 \times 10^{-20}\,m^2\,V^{-2}$, $a_2 = 0.0277 \times 10^{-40}\,m^4\,V^{-4}$, i.e. for $\eta = a_2/a_1^2 \simeq 0.11$. The measurement technique has been described by Fugiel and Westwański (1990a). The inset shows the schematic portrayal of the definition of invariant $Q = \chi_0/\chi_M$.

separate paper, where we also showed that the critical invariant (see below) $\eta = a_2/a_1^2 = 5C_2C_6/81C_4^2$ is related to the constant positive coefficients $\frac{1}{2}C_2$, $\frac{1}{4}C_4$ and $\frac{1}{6}C_6$ of the corresponding singular free energy of more general form than given in equation (4). The susceptibility $\chi(\tau, E)$ in the non-ordered phase should be an even function of E because free energy is an even function of P. For these reasons, in this paper we have considered the function $G(\chi_0/\chi)$ (instead of $G(\chi_0/\chi)^{1/2}$), for which the fitting of non-linearity to the series in variable $y = E^2\chi_0^{2h}$ is natural. In the opposite case, the fitting of the function $G(\chi_0/\chi)^{1/2}$ to the series $(a_1z + a_2z^2 + \ldots)$ of its natural variable $z = E\chi_0^h$ has no physical meaning because the susceptibility $\chi(\tau, E)$ would not be an even function of E.

A certain knowledge of the scaling function gives the opportunity of obtaining a considerable amount of information on the critical behaviour. Unfortunately, to the best of our knowledge this function is known only for the non-ordered phase in the mean-field approximation ($b = 0$ in equation (5)) (cf also Cach *et al* 1982) and for the free energy (4) (see equation (5)). Hence equation (6) is of particular significance. In order to check the suitability of equation (6) it is convenient to introduce a parameter $\eta = a_2/a_1^2$ which is a measure of deviation from the Landau theory, for which $\eta = 0$. Interesting results are obtained when comparing values of η with those of another

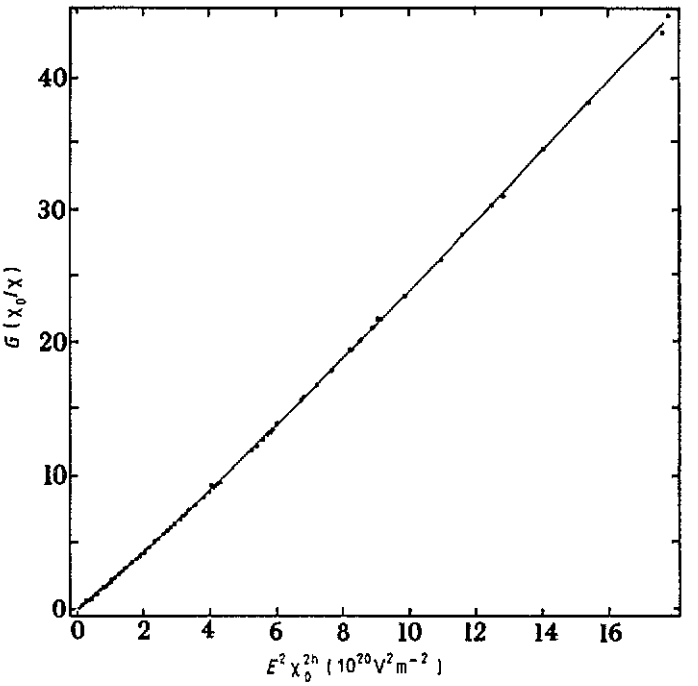

Figure 2. $G(\chi_0/\chi)$ versus $E^2\chi_0^{2h}$, where $h = \delta/(\delta - 1) = 1.46$ and $\delta = 73/23$ for TGS. Values of χ_0 were determined at 18 temperatures in the interval corresponding to $10^{-3} < (T - T_c)/T_c < 10^{-2}$ at atmospheric pressure. The susceptibility χ was determined for each of 18 temperatures for about nine values of field E. The full curve is the numerical fit according to equation (6) for $a_1 = 2.17 \times 10^{-20}\,m^2\,V^{-2}$, $a_2 = 0.0197 \times 10^{-40}\,m^4\,V^{-4}$, i.e. for $\eta = a_2/a_1^2 = 0.004$.

parameter Q, which may be defined by the relation $Q = \chi_0/\chi_M$, where χ_M is the maximum value of paraelectric susceptibility in an external electric field E applied parallel to the ferroelectric axis and χ_0 the susceptibility at $E = 0$, at the same temperature (see inset to figure 1). It has been proved (Westwański and Fugiel 1991) that the quantity Q is a universal constant (independent of external field and temperature) at the extrema of non-zero-field susceptibility, specific heat and correlation function for any physical system behaving according to the scaling hypothesis. This result is extended (Fugiel and Westwański 1991) to the case of dynamic susceptibility and discussed using the example of the Debye model.

On the basis of equation (6) and for the condition $\partial\chi/\partial T = 0$, where χ is the paraelectric susceptibility at $E \neq 0$, we obtain the following relationship between η and Q:

$$\eta = [(\varepsilon - 1)Q^2 - Q + 2][(2 - \varepsilon)Q^2 + 2Q - 4]^{-2}(Q + 2)^{-1} \qquad (7)$$

where $\varepsilon = 3(\delta - 1)/2\delta = 3\gamma/2\Delta$. As may be seen, the expression relating η and Q contains the critical exponent δ, which may also be determined from measurements outside the critical isotherm (Fugiel and Westwański 1990a), when assuming the correctness of the scaling hypothesis, i.e. making use of the formula $\delta = (\Delta/\gamma - 1)^{-1}\Delta/\gamma$. Since δ and Q are critical invariants, then from equation (7) it is clear that η is also a critical invariant. Equation (7) is a further example of the rule, known from the scaling

Table 1. Experimental data on δ (partly taken from the paper by Fugiel and Westwański (1990a)), Q and η for the ferroelectrics TGS and TGSe. Corresponding values for the Landau theory are shown for comparison.

	δ	Q	η
TGSe	3.1–3.3	1.4–1.6	0.1–0.2
TGS	3.05–3.3	1.8–1.9	0–0.02
Landau theory	3	2	0

hypothesis and confirmed by the renormalization group method, according to which two independent invariants are sufficient to determine the remaining invariants. The invariant Q has been measured experimentally for TGS (Westwański and Fugiel 1991) and TGSe (Fugiel and Westwański 1990b) crystals and the values of Q were found to lie between the Landau critical ($Q = 2$) and tricritical ($Q = \frac{4}{3}$) point values. The susceptibility scaling functions and invariant Q for Landau critical and tricritical points above and below T_c are discussed in a separate paper. In table 1 are presented the intervals in which lie the most probable values of δ, Q and η obtained from experimental tests on several TGS and TGSe samples. Some of the data for δ in TGSe was also found at pressures differing from atmospheric pressure (Fugiel and Westwański 1990a) and agreeing with the results at atmospheric pressure.

If we substitute in (7) values from table 1 taken from the middle of the given intervals. i.e. $\delta = 3.2$, $Q = 1.5$, for TGSe, and $\delta = 3.18$, $Q = 1.85$, for TGS, we obtain $\eta = 0.12$ for TGSe and $\eta = 0.007$ for TGS. Thus there is good agreement between the experimental values of η shown in table 1 and the values calculated from (7) making use of the experimental data for δ and Q. Greater deviations from the Landau theory found in the values of Q for TGSe are accompanied by correspondingly greater deviation in η-values, in comparison with the corresponding parameters for TGS.

3. Conclusions

From the discussion presented above, it may be concluded that equation (6) not only permits non-Landau values of critical exponents but also, unlike (5), explains the deviation from the Landau critical point value $Q = 2$.

In this paper we have tried to demonstrate the superiority of equation (6) over equation (5) which was derived from the free-energy equation (4). It is obvious that the form of the free-energy equation given in (2) has similar if not even greater drawbacks than the form in equation (4). If we take as the starting point the free energy (2), then for the non-ordered phase we obtain the relation

$$G(\chi_0/\chi) = 27\beta_0[1 - 3b\ln(\tau/\tau_0)]^{-1}E^2\chi_0^3 \tag{8}$$

where $\chi_0 = 1/\alpha_0\tau q(\tau)$ with $q(\tau)$ defined below equation (2). Instead of the non-linear scaling function (6), in equation (8) we have to deal with a whole family of straight lines which additionally are not coincident; this does not agree with experiment.

Nevertheless, it should not be anticipated that the approximation (6) is satisfactory in the immediate vicinity of the critical point, i.e. for $y \to \infty$, i.e. $\tau \to 0$. In this case the quadratic multinomial in y appearing on the right-hand side of equation (6) should be

better replaced by an infinite series. The quadratic in y found in equation (6), however, proves to be of great significance and sufficient to explain the deviations from Landau theory presented in table 1. It may be asserted that the scaling function (6), shown to be considerably more satisfactory than function (5), gives a good description of TGS and TGSe in the neighbourhood of $T_M(E)$ and above $T_M(E)$, where $T_M(E)$ is the temperature at which the paraelectric susceptibility in the electric field E reaches a maximum.

We have then shown that in addition to the exponent ratio method (Δ/γ) (Fugiel and Westwański 1990a) for determining experimental scaling function, it is very useful to apply the described non-linearity method based on investigation of non-linearities produced by the experimental scaling function (χ/χ_0 versus $E\chi_0^{\Delta/\gamma}$) inserted into equation (5) for the susceptibility scaling function for the Landau critical point ($b = 0$). The invariant Q is a measure of non-linearity. The greater the non-linearity of the function $G(\chi_0/\chi)$ versus $y = E^2\chi_0^{2h}$, the larger is the deviation of invariant Q from the classical value $Q = 2$ for the Landau critical point. If non-linearity is convex as in figure 1 and figure 2, then Q is less than 2; if it is concave, then Q is greater than 2.

We have also investigated the susceptibility scaling function below the critical point for TGS and TGSe ferroelectrics. The experimental relation for χ/χ_0 versus $E\chi_0^{\Delta/\gamma}$ obtained in the ferroelectric phase is characterized by a larger scatter of measurement points than for the analogous relation in the paraelectric phase. Hence the estimation of exponent ratio Δ/γ has a greater error. This has meant that up to now the analysis of the susceptibility scaling function in the ferroelectric phase is insufficiently accurate.

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