this assumption is not valid. However, in this case the number of Mn atoms remains constant throughout the concentration range, and therefore we expect the number of magnetic d electrons to remain more or less constant.

[23]V. Heine, Phys. Rev. 153, 673 (1967).

[24]R. C. Wayne and L. C. Bartel, Phys. Letters 28A, 196 (1968).

[25]J. B. Goodenough, J. Appl. Phys. 39, 403 (1968).

[26]L. C. Bartel, J. Appl. Phys. 41, 5132 (1970).

[27]R. W. Lynch, J. Chem. Phys. 47, 5180 (1967).

[28]E. P. Wohlfarth (unpublished).

[29]L. C. Bartel and E. P. Wohlfarth, Bull. Am. Phys. Soc. 16, 351 (1971).

[30]If we assume a ratio I/I_b for MnSb, then I/I_b is fixed, through Eq. (3), for the solid solutions when $x>0$. The results shown in Fig. 7 are independent of the assumed value of I/I_b for MnSb.

[31]The lattice parameters for MnSb and MnAs at $T = 20$ °C were taken from the work of B. T. M. Willis and H. P. Rooksby, Proc. Phys. Soc. (London) 67B, 290 (1954). To obtain values for the intermediate solid solutions a linear extrapolation was used as the data of Ref. 3 suggest.

[32]For $ZrZn_2$, the Fermi level lies at the peak in the density of states that has a full width of approximately 0.16 eV [G. S. Knapp, F. Y. Fradin, and H. V. Culbert, J. Appl. Phys. 42, 1341 (1971)].

[33]J. B. Goodenough (private communication).

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Critical Region in Ferroelectric Triglycine Sulfate

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Careful measurements have been made for triglycine sulfate (TGS), in the vicinity of the critical point T_c, on the temperature dependence of the spontaneous polarization and the field dependence of the polarization at T_c. It is found that deviations from the mean-field theory occur only within $T_c - T < \Delta T_c \approx 5\times10^{-3}$ °C and $E < E_c \approx 0.5$ V/cm. The coherence length ξ_0 at 0°K is calculated on the basis of Menyhárd's theory, which gives a condition for the breakdown of the mean-field theory. The minimum values of ξ_0 obtained by ΔT_c and E_c are 7 and 6 Å, respectively, which are very close to the average distance, 6.8 Å, between statistical units of TGS.

The behavior of ferroelectric crystals near the critical temperature is of much interest, because it is typical of the cooperative phenomena in which the long-range electrostatic interaction plays an important role. Recent studies on triglycine sulfate (TGS) have shown that the experimental results are well explained by the Weiss-type mean-field theory (classical theory) in the range of $|T - T_c| \gtrsim 3\times10^{-2}$ °C and $E \gtrsim 30$ V/cm, where E is an applied electric field.[1,2] Furthermore, Blinc suggested that inside these regions the value of critical exponents obtained by hysteresis measurements were very close to those predicted by the three-dimensional Ising model.[2] The careful measurement of the dielectric constant[3] shows, however, that the critical exponent has the classical value even at $T - T_c = 10^{-2}$ °C and -5×10^{-3} °C. The aim of this note is to report the results of careful measurements of the dielectric hysteresis and to examine the range of validity of the mean-field theory in the vicinity of the critical point.

The samples used in the present measurements were gold evaporated on both b surfaces. The 50-Hz hysteresis loops were displayed on the oscilloscope screen through a Sawyer-Tower circuit with phase compensation. The values of spontaneous polarization P_s were determined by photographs enlarged about four times. The experimental setup was almost the same as that previously reported.[3] Measurements were made in the cooling process

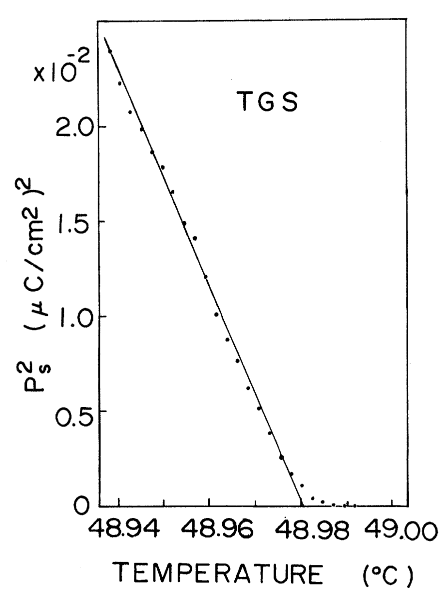

FIG. 1. Square of the spontaneous polarization vs temperature in TGS in the very vicinity of the Curie point.

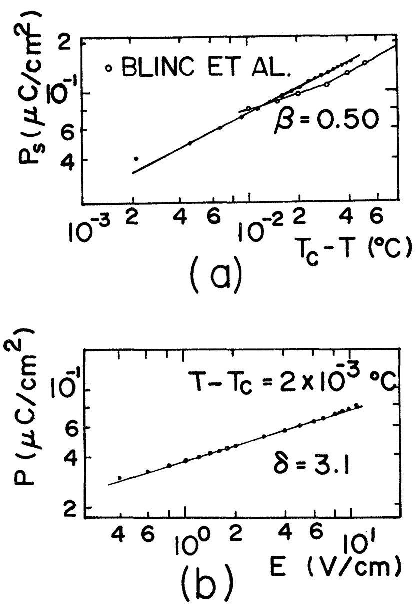

FIG. 2. (a) Log-log plot of spontaneous polarization vs $T_c - T$. (b) Log-log plot of polarization vs applied electric field at $T - T_c = 2\times10^{-3}$ °C.

at a rate of about 0.002 °C/min.

In Fig. 1 we show the square of the spontaneous polarization vs temperature. The peak value of the applied external field was 10 V/cm. A linear relationship holds below $T - T_c \approx -5\times10^{-3}$ °C. Here T_c is the temperature obtained by extrapolation of the linear relationship. Then the critical exponent β defined by

$$P_s \propto (T_c - T)^{\beta}$$

is in good agreement with the classical value $\frac{1}{2}$ in this temperature range. This agrees with the range obtained by dielectric-constant measurements.[3] The log-log plot of P_s vs $T_c - T$ is shown in Fig. 2(a). The results reported by Blinc *et al.*[2] are also shown for comparison. Unlike the results obtained by Blinc *et al.*, the "classical" region extends at least to 5×10^{-3} °C.

The log-log plots of polarization P vs E for the same specimen at $(T_c + 0.002)$ °C are shown in Fig. 2(b). From the gradients of the curves we can obtain the critical index δ which is defined as

$$P \propto E^{1/\delta}$$

at the critical temperature. Since the critical temperature is expected to be very close to, but slightly above, T_c, it can be concluded from Fig. 2(b) that the value of δ is almost the same as the classical value 3.0, above about 0.5 V/cm.

From the results stated above, we may reasonably conclude that the critical region of TGS is within the ranges of $|T - T_c| < 5\times10^{-3}$ °C and $|E| < 0.5$ V/cm in the $E \sim T - T_c$ plane. Recently, Menyhárd[4] has shown, on the basis of the Landau theory, that the boundary of the critical region, where deviation from the classical theory becomes remarkable, can be given as

$$E = \pm E_c\left(1 + \frac{T - T_c}{\Delta T_c}\right)\left(1 - \frac{T - T_c}{2\Delta T_c}\right)^{1/2}, \qquad (1)$$

with

$$\Delta T_c \approx 10^{-3} k^2 T_c (\Delta C)^{-2} \xi_0^{-6} \qquad (2)$$

and

$$E_c \approx 10^{-5} k^3 T_c (\Delta C)^{-2} P_s(0) \xi_0^{-9}, \qquad (3)$$

where ΔC is the jump of the specific heat at T_c calculated by the Weiss theory and ξ_0 and $P_s(0)$ are, respectively, the coherence length and the spontaneous polarization extrapolated to 0 °K. Inserting suitable values[5] for T_c, ΔC, and $P_s(0)$ into (2) and (3), and putting $\Delta T_c = 5\times10^{-3}$ °C and $E_c = 5\times10^{-1}$ V/cm, we obtain $\xi_0 \approx 7$ Å from (2) and $\xi_0 \approx 6$ Å from (3). These values are very close to an average distance r_0 between statistical units in TGS given by

$$r_0 = (V/Z)^{1/3} \approx 6.8 \text{ Å},$$

where V is the unit-cell volume and Z is the number of the formula units per unit cell.

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[1] J. A. Gonzalo, Phys. Rev. Letters 21, 749 (1968); Phys. Rev. B 1, 3125 (1970).

[2] R. Blinc, M. Burgar, and A. Levstik, Solid State Commun. 8, 317 (1970).

[3] E. Nakamura *et al.*, J. Phys. Soc. Japan Suppl. 28, 271 (1970).

[4] N. Menyhárd, Solid State Commun. 8, 1337 (1970).

[5] F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, London, 1962).