Dielectric-constant logarithmic correction in RbH_2PO_4 above the Curie point

José L. Martínez and Julio A. Gonzalo
Departamento Optica y Estructura de la Materia, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid 34, Spain and Instituto de Física del Estado Sólido del Consejo Superior de Investigaciones Científicas (CSIC-UAM), Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid 34, Spain
(Received 27 April 1984; revised manuscript received 1 November 1984)

Dielectric-constant measurements in rubidium dihydrogen phosphate at frequencies from 20 Hz to 10 kHz, within an interval of about ±30 K from the Curie point, have been performed with a digital universal bridge. The relative accuracy of capacitance readings was better than 0.1%. Asymptotically close to $T_c = 145.90 \pm 0.02$ K and within an interval of 20 K above T_c, the data appear to follow reasonably well a Curie-Weiss law with logarithmic corrections, first predicted by Larkin and Khmel'nitskii for uniaxial ferroelectrics, and then change over gradually to normal Curie-Weiss behavior.

I. INTRODUCTION

Rubidium dihydrogen phosphate (RbDP), a well-known ferroelectric isomorph of potassium dihydrogen phosphate (KDP), shows a second-order phase transition at $T_c \approx 146$ K at ambient pressure. Its dielectric, thermal, structural, and lattice-dynamical properties have been extensively studied.[1–9] The second-order character of the transition, in contrast to that of KDP, is generally agreed upon, while at the same time its proximity to a tricritical point is stressed.

In their 1969 paper[10] on phase transitions of uniaxial ferroelectrics, Larkin and Khmel'nitskii (LK) predicted logarithmic corrections to classical (Curie-Weiss) behavior of the dielectric constant and other anomalous physical properties near T_c, suggesting specifically triglycine sulfate (TGS) and RbDP to test their theory. Logarithmic corrections in the specific heat of TGS have been observed recently by Ema,[11] but no such corrections have been unambiguously observed in the dielectric constant for this crystal as far as we know. Recent dielectric constant measurements by Sandvold and Courtens[12] on tris-sarcosine calcium chloride produced a good fit to an empirical expression including logarithmic corrections compatible with LK theory. No clear crossover to normal Curie-Weiss behavior was discernible above T_c from these data.

II. EXPERIMENTAL

The samples were cut from a single crystal grown from water solution in the form of plates of $4 \times 4 \times 0.5$ mm^3 with the main surfaces perpendicular to the polar c axis. Gold-leaf electrodes were directly attached to the main surfaces. The sample holder was located within the evacuated cavity of a cryostat filled with liquid N_2. The slow spontaneous heating technique was used in which the rate of heating of the evacuated sample cavity was governed by liquid-nitrogen evaporation at a rate of about 0.5 K/min. At regularly spaced time intervals we measured the capacitance and loss factor (by means of an ESI universal video bridge) and the sample thermocouple temperature (by means of a Fluke microvoltmeter). The relative precision of the capacitance measurements was always better than 0.1% and the relative precision of temperature readings better than 0.02 K. The residual capacitance of the system to be subtracted from capacitance readings was carefully determined using a set of single-crystal cleaved plates of NaCl of 0.5 mm thickness and of varying area provided with gold-leaf electrodes, and extrapolating linearly C for A (area)$\rightarrow 0$, obtaining 7.1 pF as residual capacitance. The field amplitude used was 1 V/cm, considered sufficiently low for this kind of measurement.

III. RESULTS

Measurements of sample capacitance and dielectric loss using an ac amplitude of 1 V were performed at the following frequencies: 20 Hz, 100 Hz, 1 kHz, and 10 kHz (all peak values fall within 5% of each other). In all cases the temperature dependence was qualitatively the same: a gradual and relatively small increase in capacitance below T_c followed by a much more pronounced decrease above T_c which did not quite fit the Curie-Weiss law in the immediate vicinity of T_c. This is illustrated by the gradually decreasing slope in ϵ^{-1} versus T just above the transition temperature shown in Fig. 1 for 1 kHz, but the same feature was observable for all other frequencies at which measurements were performed. Rounding due to impurity-induced small bias or thermal gradients should show up as a bend in the slope in the opposite direction. Previous work on RbDP by Gladkii and Sidnenko[1] and by Peercy and Samara[4] do not show evidence of logarithmic correction. On the other hand, our data contain many more points per degree, and the bending of our data points for ϵ^{-1} versus T is directly visible in a linear plot only in an interval of about 5 K above T_c. Roughly speaking the width of the critical region should be of this order.

It may be pointed out that the peak value of the dielectric constant in our data is substantially lower than others[2–4] previously reported. This might be due to lower

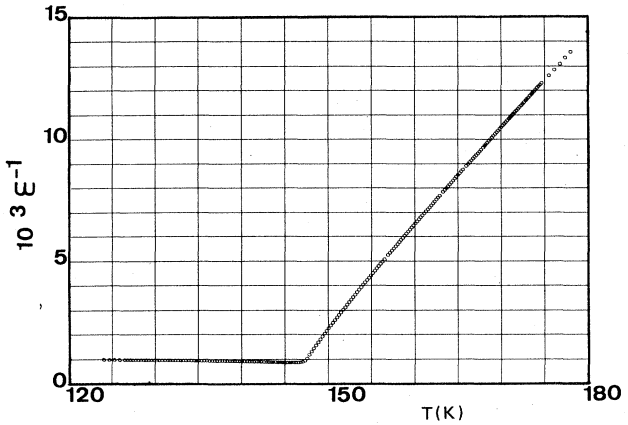

FIG. 1. Inverse dielectric constant vs temperature for RbH_2PO_4 ($F=1$ kHz, $V=1$ volt rms).

sample quality but in any case impurities and/or defects usually give rise to bending of the $\epsilon^{-1}(T)$ curve in the opposite direction.

IV. DISCUSSION

We have tried to fit the behavior of $\epsilon^{-1}(T)$ above the transition to the expression of LK (Ref. 10) which can be written as

$$\epsilon^{-1}=(\Delta T/C)[1+g\ln(\Delta T_0/\Delta T)]^{-1/3}\,, \tag{1}$$

where $\Delta T=T-T_c$, C=Curie constant above T_c, and g and ΔT_0 are characteristic parameters of the material undergoing the second-order phase transition. Equation (1) can be rewritten as

$$\epsilon^{-1}=\frac{\Delta T}{C[1+g\ln\Delta T_0]^{1/3}}\left[1-\left[\frac{g}{1+g\ln\Delta T_0}\right]\ln T\right]^{-1/3}$$
$$=\frac{\Delta T}{C'}[1-g'\ln\Delta T]^{-1/3}\,. \tag{2}$$

To determine the possible presence of the logarithmic correction term in our data the most sensitive parameter by far is T_c. To perform a preliminary determination of T_c, weighting properly the data closer to the transition, one can use the following procedure: Assuming that a power law $\epsilon^{-1}\approx A(\Delta T)^{\gamma}$ is approximately fulfilled, one can plot the ratio $[\epsilon^{-1}/(d\epsilon^{-1}/dT)]$ versus temperature. If the assumption is correct one obtains a linear plot, and from the extrapolation to $\epsilon^{-1}=0$ one obtains T_c directly. We followed this procedure with our data, obtaining $T_c=145.90$ K. Using this T_c with selected data for ϵ^{-1} encompassing an interval of 12 K above the transition (at higher temperatures a trend towards normal Curie-Weiss behavior is discernible) one can easily estimate the other parameters, $g'\approx-0.860$ and $C'\approx1420$. These parameter values were subsequently used as initial values in a computer fit of Eq. (2) in which T_c, g', and C' were left free to change, to the full set of data for $\epsilon^{-1}(T)$ in the whole temperature interval omitting only the first three points corresponding to nearly flat ϵ^{-1} very near T_c. The parameters thus obtained were $T_c=145.85$ K, $g'=-0.86$, and $C'=1425.36$. The semilogarithmic plot in Fig. 2 shows the good fit of the theoretical expression for $\epsilon^{-1}(T)$, with the experimental values. At temperatures for which $\Delta T\geq12$ K, the data appear to show a gradual tendency towards Curie-Weiss behavior, which is slightly enhanced if one subtracts from the ϵ value $\epsilon_0\approx4.5\pm1.5$ estimated from room-temperature measurements. Taking into account that the value for the Curie constant C obtained from our data for $12\leq\Delta T\leq40$ K is $C=2.546\times10^3$ (lower by 13% than some previously reported[1]) one can obtain from

$$C'=C(1+g\ln T_0)^{1/3}=1425.36\,, \tag{3}$$

$$g'=g(1+g\ln T_0)^{-1}=-0.86\,, \tag{4}$$

the corresponding values for the parameters in the LK expression

$$g\approx(-0.150)\ \text{(dimensionless)}\,, \tag{5}$$

$$\Delta T_0\approx237\ \text{K}\,. \tag{6}$$

According to this, the value of g is small and negative[13] and there would be a change of sign in the product $(g'\ln\Delta T)$ in Eq. (2) at $T=T_0=237$ K above T_c, which, probably by a fortuitous coincidence, happens to fall very close to the next high-temperature transition in RbDP (from tetragonal to monoclinic) which takes place at $T=86°$C. A negative g implies a divergence of ϵ^{-1} above T_c at $\Delta T=\Delta T_0\exp(1/g)$, in our case at $\Delta T\simeq0.2$ K which is located in the critical region, below the temperature where $(\epsilon^{-1})_{\text{exp}}$ becomes nearly flat, corresponding to experimental points excluded from our fit.

LK state in their paper[10] that Eq. (1) is applicable for displacive-type transitions, whereas $\epsilon\sim|T-T_c|^{-1}\times\ln^{1/3}|T-T_c|$ is applicable for order-disorder—type transitions. RbDP is generally considered to show an order-disorder—type transition, like its isomorphs at ambient pressure, but there is also experimental evidence[4,14] that it presents an underdamped soft-mode indicative, at least partially, of a displacive-type character of the transi-

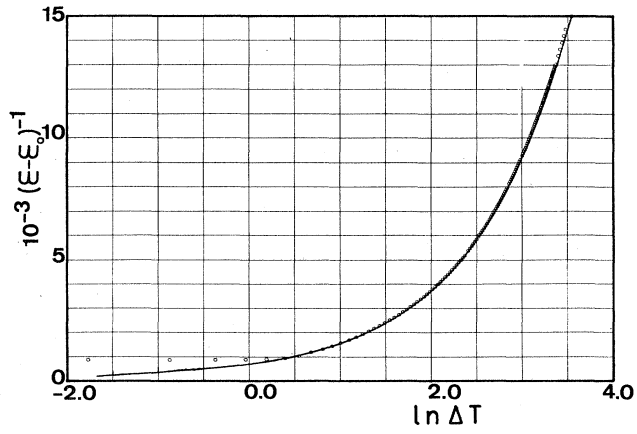

FIG. 2. Semilogarithmic plot of $(\epsilon-\epsilon_0)^{-1}$ vs T for RbH_2PO_4. The theoretical curve is the LK expression [Eqs. (1) and (2)] with $T_c=145.85$, $g'=-0.86$, $C'=1425.36$, and $\epsilon_0=3.5$ (solid curve). Points are experimental data.

tion. In fact, the existence of double potential-well minima separated by energy barriers does not exclude the possibility of relative displacements of these minima, accompanied by changes in the height of the barrier, which could give the transition a mixed (order-disorder)-(displacive) character. Thus, the applicability of Eq. (1) to the RDP transition should not be ruled out entirely on the grounds of its having order-disorder character.

The mean deviation

$$R=(1/N)\sum_{i=1}^{N}|\epsilon_{i\,\mathrm{expt}}^{-1}-\epsilon_{i\,\mathrm{calc}}^{-1}|/\epsilon_{i\mathrm{calc}}^{-1}$$

for the logarithmic correction fit was $R_{LC}=0.0037$, clearly better than the deviation for a power law $(\epsilon^{-1}\approx A(\Delta T)^{\gamma})R_{\mathrm{PL}}=0.0075$. Attempts to fit our data with Curie-Weiss and power laws using background terms linear in temperature gave definitely inferior fits to those obtained with a logarithmic correction.

ACKNOWLEDGMENT

We wish to thank L. Montoto and M. Aguilar for their help with the computer fitting of the experimental data.

[1]V. V. Gladkii and E. V. Sidnenko, Fiz. Tverd. Tela (Leningrad) **13**, 1642 (1971) [Sov. Phys.—Solid State **13**, 1374 (1971)]; see also M. Amin and B. A. Strukov, Fiz. Tverd Tela **10**, 3148 [**10**, 2498 (1969)].

[2]C. Pierre, J. P. Dufour, and M. Remoissenet, Solid State Commun. **9**, 1493 (1971).

[3]B. A. Strukov, A. Baddur, V. N. ZInenko, A. V. Mishchenko, and V. A. Koptsik, Fiz. Tverd. Tela (Leningrad) **15**, 1388 [Sov. Phys.—Solid State **15**, 939 (1973)].

[4]P. S. Peercy and G. A. Samara, Phys. Rev. B **8**, 2033 (1973).

[5]P. Bastie, J. Lajzerowicz, and J. R. Schneider, J. Phys. C **11**, 1203 (1978).

[6]F. Troussaut, P. Bastie, J. Bornarel, and M. Vallade, Ferroelectrics **39**, 1053 (1981).

[7]P. Schnackenberg, J. Pipman, V. H. Schmidt, and G. F. Tuthill, Ferroelectrics **39**, 1045 (1981).

[8]V. H. Schmidt, P. T. Schnackenberg, A. B. Western, A. G. Baker, C. R. Bacon, and W. P. Crummett, Ferroelectrics **24**, 275 (1980).

[9]K. Gesi, K. Ozawa, T. Osaka, and Y. Makita, J. Phys. Soc. Jpn. **52**, 2538 (1983).

[10]A. I. Larkin and D. E. Khmel'nitskii, Zh. Eksp. Teor. Fiz. **56**, 2087 (1969) [Sov. Phys.—JETP **29**, 1123 (1969)].

[11]K. Ema, J. Phys. Soc. Jpn. **52**, 2798 (1983).

[12]E. Sandvold and E. Courtens, Phys. Rev. B **27**, 5660 (1983).

[13]The negative value of g is somewhat unexpected. According to LK, however, $g\equiv 3\gamma=T_c bv/32\pi(\lambda s^3)^{1/2}$, and, even if all the quantities involved are positive, the square root implies a $\pm$ sign compatible with a negative g value. On the other hand, a reasonably good fit can be obtained using $C=2250$, a positive $g=0.05$, $\Delta T_0=20$ K, and $T_c=145.2$ (corresponding to $g'=0.0435$ and $C'=2357$), which presents a divergence at $\Delta T\simeq 9.7\times 10^9$, very far from T_c. The quality of the fit with this set of parameters in an interval of $\Delta T\simeq 20$ K above T_c is, however, definitely inferior to that obtained using a negative $g=-0.86$ and $C'=1425$, as indicated by a mean deviation (R) about ten times larger in the former case.

[14]P. S. Peercy, Phys. Rev. Lett. **31**, 379 (1973).