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Dielectric relaxation in pseudo-one-dimensional ferroelectric CsD_2PO_4

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Dielectric dispersion in pseudo-one-dimensional hydrogen-bonded ferroelectric CsD_2PO_4 was measured in the frequency range from 100 kHz to 2 GHz for temperatures between -13 and 30 °C. The observed relaxation is monodispersive in the paraelectric phase, except in the vicinity of the transition. The static dielectric constant ϵ_s shows classical critical behavior, with the critical coefficient $\gamma = 1$. The relaxation frequency f_ϵ is much lower than in corresponding three-dimensional systems and exhibits a pronounced critical slowing down with a nonclassical exponent of 1.3. Outside the critical region in the paraelectric phase, ϵ and f_ϵ can be described reasonably well by a pseudo-one-dimensional Ising model, treating the interchain interactions in the mean-field approximation. The intrachain and interchain interactions obtained agree well with previously determined values. The noninteracting deuteron intrabond-jump time is much smaller than in KD_2PO_4 but has the same activation energy.

I. INTRODUCTION

Cesium dihydrogen phosphate CsH_2PO_4 (CDP), along with its deuterated isomorph CsD_2PO_4 (DCDP), is a well-known example of a pseudo-one-dimensional hydrogen-bonded ferroelectric crystal.[1-12] The crystal is monoclinic[4] (space group $P2_1/m$) with two formula units per primitive unit cell in the high-temperature paraelectric phase. There are two different types of O—H · · · O bonds in the structure.[4,13] The O—H(1) · · · O bonds link the PO_4 groups along the a axis and are ordered even in the high-temperature phase. The O—H(2) · · · O bonds, on the other hand, form zigzag chains along the ferroelectric b axis and are disordered in the paraelectric phase and become ordered only below the transition temperature in the ordered, ferroelectric phase.[6,8,9,11,13] Neutron scattering studies[6,9,12] of DCDP showed that diffuse scattering in the paraelectric phase is characteristic of a one-dimensional system with chainlike ordering parallel to the b axis. Only close to the transition temperature T_c do the three-dimensional fluctuations become important,[9,12] but the correlations are still much longer ranged along the chain direction than along the other two directions. CDP is therefore a quasi-one-dimensional system.

The observed ordering of O—H(2) · · · O bonds and the rather large isotope effect[2] in T_c upon deuteration ($T_{c,\mathrm{D}}/T_{c,\mathrm{H}} = 1.74$) demonstrate the role of the O—H(2) · · · O hydrogen bonds in the transition. Therefore, one can think of CDP as a one-dimensional version of KH_2PO_4, where the disordered hydrogen-bond network is three dimensional,[14] and a quasi-one-dimensional Ising model in a transverse tunneling field can be an appropriate microscopic model of CDP. Just as in KD_2PO_4,[14] the tunneling effects can probably be neglected in DCDP, and one is left with a simple anisotropic (quasi-one-dimensional) Ising model with strong intrachain ($J_{\|}$) and weak interchain ($J_{\perp}$) interactions,

$$\mathscr{H} = -J_{\|} \sum_{x,y,z} \sigma(x,y,z)\sigma(x,y+1,z) - \sum_{\substack{x,x',y,y',z,z' \\ (x,z)\neq(x',z')}} J_{\perp}(x-x',y-y',z-z')\sigma(x,y,z)\sigma(x',y',z') \ . \quad (1)$$

Here y corresponds to the intrachain coordinate (along the b axis) and x,z describe the two coordinates of the chain. σ is the spin-$\frac{1}{2}$ operator and its two possible values $\sigma = \pm 1$ represent the position of the deuteron in one of the two possible equilibrium sites in the O—H(2) · · · O bond.

DCDP therefore represents an ideal system for testing some exact and approximate results of the quasi-one-dimensional Ising model for static and especially dynamic quantities. The simplest approximation for analyzing the static properties of the quasi-one-dimensional Ising model [Eq. (1)] is the linear-chain approximation (LCA), in which the interchain interactions are treated as a mean field, while the intrachain interactions are taken into account rigorously.[15,16] The above model yields in the linear-chain approximation the following expression for the static dielectric constant above T_c ($T > T_c$):

$$\epsilon_s = \frac{A}{T}\left[\exp\left[-\frac{2J_{\parallel}}{T}\right] - \frac{J_{\perp}}{T}\right]^{-1} . \tag{2}$$

Here all the parameters are in temperature units,

$$J_{\perp} = \sum_{\substack{x,y,z \\ (x,z)\neq(x',z')}} J_{\perp}(x-x',y-y',z-z')$$

and $A = N\mu^2$, N being the number of O—H(2) $\cdots$ O hydrogen bonds per unit volume and μ the effective dipole moment of a hydrogen bond.

The measured static dielectric constant of DCDP can be satisfactorily described by expression (2) over the whole temperature region above T_c,[8] showing a crossover between a one-dimensional regime far away from T_c and a classical three-dimensional regime close to T_c with the critical exponent $\gamma = 1$. Expression (2) can be also used to fit the neutron scattering data.[12] The parameters of the system, i.e., $J_{\parallel}$ and $J_{\perp}$ determined from neutron scattering data,[12] agree fairly well with the ones obtained from dielectric measurments.[8] The two intrachain coupling constants $J_{\parallel}$ are practically equal, while $J_{\perp}$ seems to depend more on the level of deuteration of the system, reproducing the dependence of T_c on deuteration.

Static dielectric measurements on DCDP show relatively large difference between the transition temperature T_c and the Curie-Weiss temperature T_0 and only small thermal hysteresis.[2,8] The difference $T_c - T_0$ is strongly sample dependent, has the values between 0.1 and 14 K,[8,17] and seems to depend on the level of deuteration and impurities in the system. One does not observe any discontinuity and rounding of ϵ at T_c but only a discontinuous change in the slope $d\epsilon/dT$.

There also exist some dynamic measurements on DCDP in which the critical dynamics are tested by deuteron magnetic resonance[11] and by measuring the dielectric relaxation.[17] Dielectric data also exist for undeuterated CDP.[17,18] All these results show directly[17,18] or indirectly[11] a pronounced critical slowing down effect near T_c, with characteristic relaxation frequencies which are much smaller (approximately 2 orders of magnitude) than in analogous three-dimensional systems (KH_2PO_4 and KD_2PO_4). The dynamic properties of DCDP are usually analyzed by a kinetic pseudo-one-dimensional Ising model[19] treated in the (LCA).[20] The measurements roughly agree with LCA results but display some systematic deviations from them close to the transition. Therefore, the dynamic parameters extracted from experimental data in such a way could be of questionable value.

We measured the dielectric dispersion in DCDP in the frequency range from 100 kHz to 2 GHz for temperatures between -13 and 30° C, and by Cole-Cole analysis determined the temperature dependence of the static dielectric constant ϵ_s and that of the relaxation frequency f_ϵ. The results were analyzed in terms of the LCA approximation.

II. EXPERIMENTAL RESULTS

The complex dielectric constant of DCDP along the ferroelectric b axis was measured with HP 8407 and HP 8410 network analyzers in the frequency range from 100 kHz to 2 GHz. The sample faces perpendicular to the ferroelectric axis were covered by vacuum-evaporated gold electrodes. The frequencies were automatically adjusted and the output data automatically recorded. The cylindrical sample was 1 mm thick and had a diameter of 1.5 mm. The temperature was changed over the interval from -13 to 30 °C and all data were taken for decreasing temperature. The temperature of the sample holder was stable to ± 0.02 K during the measurements at various frequencies. The crystals were grown by slow evaporation of a heavy water solution of cesium carbonate and phosphorous pentoxide ($Cs_2CO_3 + P_2O_5 + 2D_2O \rightarrow 2CsD_2PO_4 + CO_2$).

In Fig. 1 the Cole-Cole plot for $T = -7.04$ °C is shown, which is typical for the region close to T_c. Away from T_c in the paraelectric phase ($T > T_c + 6$ K), the relaxation is monodispersive but becomes polydispersive closer to T_c in the paraelectric and in the ferroelectric phase. In the ferroelectric phase an additional low-frequency ($\sim$0.3-MHz) dispersion attributed to domain-wall motion was observed. The transition temperature T_c was determined as the temperature where this low-frequency dispersion disappears. The transition temperature T_c of the sample was -7.9 °C, a little larger than in previous studies,[8,12] indicating more complete deuteration of the crystal. The $\epsilon(\omega)$ data were analyzed with the Cole-Cole formula

$$\epsilon(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (i\omega\tau_\epsilon)^{1-h}} , \tag{3}$$

where $\epsilon(\omega)$ is the complex dielectric constant as a function of angular frequency ω, ϵ_s is the static

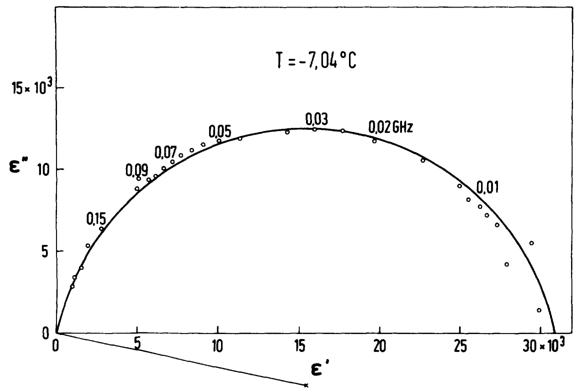

FIG. 1. Cole-Cole diagram of DCDP close to T_c in the paraelectric phase.

dielectric constant, ϵ_∞ is the high-frequency dielectric constant, τ_ϵ the dielectric relaxation time, and $\beta = 1-h$ is the dispersion parameter. ϵ_∞, which is much smaller than $\epsilon(\omega)$, does not influence the analysis and cannot be accurately determined.

In Fig. 2 the temperature dependence of the dispersion parameter β is shown. β equals one except in the polydispersive region close to T_c. Even there $\beta \simeq 1$, demonstrating that the relaxation is approximately monodispersive. A small discontinuity of β at T_c could be an indication that the transition is slightly first order.

The inverse static dielectric constant ϵ_s^{-1} as a function of temperature is presented in Fig. 3. In agreement with previous study[8] ϵ_s^{-1} shows linear behavior close to $T_c = 265.2$ K ($T < T_c + 5$ K). In this region the static dielectric constant can be represented by the Curie-Weiss law

$$\epsilon_s = \frac{C}{T - T_0}\,, \tag{4}$$

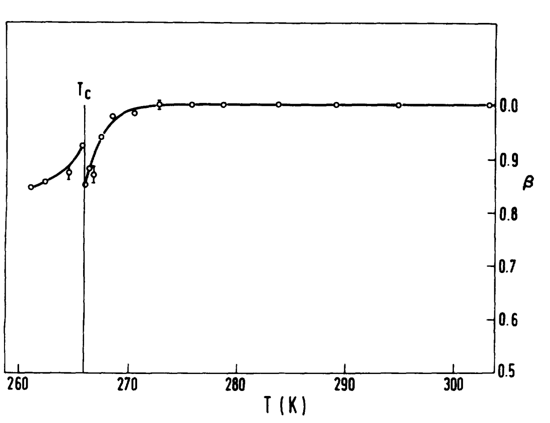

FIG. 2. Temperature dependence of the dispersion parameter β of DCDP. For $T > 275$ K, the size of the points is approximately equal to the experimental error.

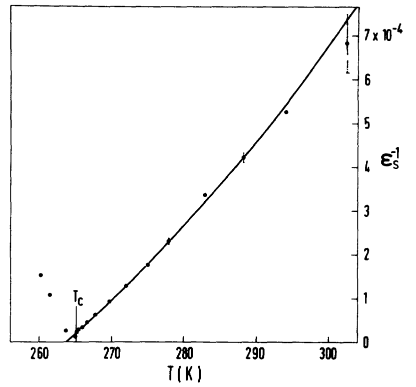

FIG. 3. Temperature dependence of the inverse static dielectric constant ϵ_s^{-1} of DCDP. The solid line represents the theoretical curve. For $T < 275$ K, the size of the points is approximately equal to the experimental error.

where the Curie-Weiss temperature T_0 was determined by extrapolation as 263.85 K, $T_c - T_0 = 1.4$ K, and the Curie-Weiss constant C equals 7.2×10^4 K, which is more than 1 order of magnitude greater than in a corresponding three-dimensional system (KD_2PO_4).[21] At higher temperatures ($T > T_c + 5$K) one observes a deviation from the Curie-Weiss behavior, in agreement with direct measurements of the low-frequency dielectric constant.[8] Similar temperature dependence with classical behavior close to T_c has also been observed in undeuterated crystals of CDP.[17] A recently observed nonlinear dependence of $\epsilon_s^{-1}(T)$ in CDP and DCDP close to the transition[18] can probably be attributed to the effect of impurities or to neglect of the difference between the transition temperature T_c and the Curie-Weiss temperature T_0 ($T_c - T_0 \simeq 0.1$ K).

The relaxation frequency $f_\epsilon = 1/2\pi\tau_\epsilon$ is presented as a function of temperature in Fig. 4. It slows down from 2 GHz at 30 °C to 13 MHz at T_c. In contrast to ϵ_s^{-1}, f_ϵ is not a linear function of T even in the neighborhood of T_c.

III. DISCUSSION

Treating the kinetic pseudo-one-dimensional Ising model[19] in the linear-chain approximation by neglecting interchain correlations, one obtains for the dielectric relaxation frequency the expression[20]

$$f_\epsilon = f\left[\cosh\frac{2J_\parallel}{T}\right]^{-1}\left[\exp\left[-\frac{2J_\parallel}{T}\right] - \frac{J_\perp}{T}\right]. \tag{5}$$

Here f is the relaxation frequency of noninteracting elementary dipoles, which consist of a deuteron in a

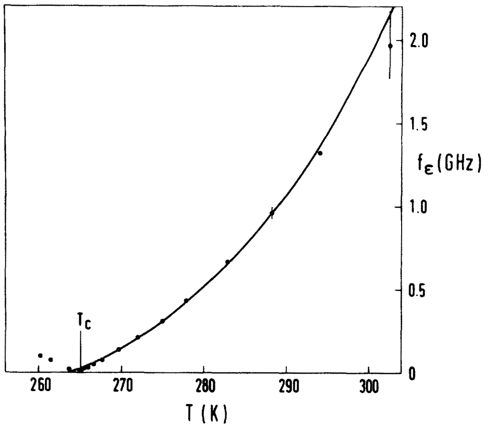

FIG. 4. Temperature dependence of the relaxation frequency f_ϵ. The solid line represents the theoretical curve. For $T<275$ K, the size of the points is approximately equal to the experimental error.

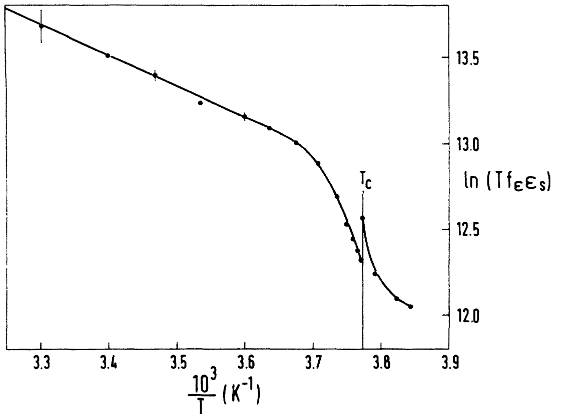

FIG. 5. Natural logarithm of the product of the kinetic coefficient $\epsilon_s f_\epsilon$ and absolute temperature (T) as a function of T^{-1}, with f_ϵ given in GHz. For $10^3 T^{-1} > 3.6$, the size of the points is approximately equal to the experimental error.

double-well potential and of heavy ions coupled to it. One usually assumes for f an exponential temperature dependence[22]

$$f = f_0 e^{-\Delta U/T} , \tag{6}$$

where ΔU is the activation energy for the reorientation of a molecular dipole and equal to the height of the barrier in the double-well potential. From expressions (2) and (5) one can get for the kinetic coefficient

$$\epsilon_s f_\epsilon = \frac{A}{T} f \left[\cosh \frac{2J_{\parallel}}{T} \right]^{-1} . \tag{7}$$

For temperatures which are much higher than $J_{\parallel}$, expression (7) reduces to

$$\epsilon_s f_\epsilon = \frac{A}{T} f_0 e^{-\Delta U/T} , \tag{8}$$

which is valid for three-dimensional ferroelectrics in the mean-field regime, and is used to determine the activation energy ΔU and f_0 from dielectric data.[22] In this case A equals the Curie-Weiss constant in the paraelectric phase..

The intrachain coupling constant $J_{\parallel}$ for DCDP is much bigger than the maximal experimentally accessible temperature,[8,12] so we are always in the low-temperature limit $2J_{\parallel} \gg T$. The expression for the kinetic coefficient [Eq. (7)] now has the form

$$\epsilon_s f_\epsilon = \frac{2A}{T} f_0 e^{-(2J_{\parallel} + \Delta U)/T} . \tag{9}$$

The factor $2\exp(-2J_{\parallel}/T)$ represents a decrease of the kinetic coefficient from its mean-field value [Eq. (8)] because of one-dimensional intrachain correlations. Figure 5 shows the natural logarithm of $T\epsilon_s f_\epsilon$ as a function of the inverse absolute temperature T^{-1}. Equation (9) is evidently valid only at high temperatures, where it corresponds to a straight line. The deviation from the straight line close to T_c is a consequence of three-dimensional interchain correlations, which are not taken into account in the derivation of Eq. (9). The temperature interval ($T - T_c \leq 7$ K) where this deviation is observed agrees with the temperature range where the nonclassical critical behavior of f_ϵ with the critical exponent 1.3 is observed (Fig. 6). Equation (5) therefore can be used for a quantitative analysis of experimental data only for $T > T_c + 7$ K.

We fitted expression (2) and the low-temperature

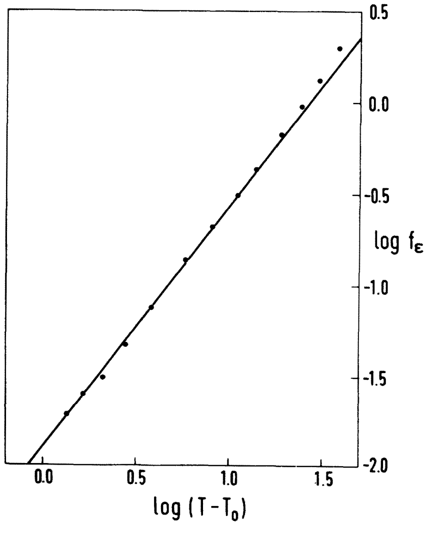

FIG. 6. Logarithm of the relaxation frequency f_ϵ (in GHz) as a function of $\log(T-T_0)$.

form of Eq. (5) ($2J_{\parallel} \gg T$),

$$f_{\epsilon}=2f_0\exp\left(-\frac{2J_{\parallel}+\Delta U}{T}\right)\left[\exp\left(-\frac{2J_{\parallel}}{T}\right)-\frac{J_{\perp}}{T}\right], \tag{10}$$

to the experimental data for ϵ_s and f_{ϵ} in the temperature interval $T_c + 7\ \mathrm{K} < T < T_c + 40\ \mathrm{K}$. This temperature range is much smaller than the one analyzed in Ref. 8, and the estimated experimental error at higher temperatures is too large to allow a complete determination of all the parameters of the model. Choosing for $2J_{\parallel}$ the value 1350 K, which is close to the values obtained from dielectric[8] ($2J_{\parallel}=1365$ K) and neutron scattering[12] ($2J_{\parallel}=1300$ K) experiments, the best fit is obtained for $J_{\perp}=1.58$ K, $A=2570$ K, $f_0=6.6\times 10^{13}$ Hz, and $\Delta U=450$ K. The calculated temperature dependences of ϵ_s^{-1} and f_{ϵ} are represented by full curves in Figs. 3 and 4.

The value for $A = N\mu^2 = 2570$ K agrees well with the one obtained from static dielectric measurements[8] (within 10%). Calculating the number of elementary dipoles per unit volume (N) from structural data,[9,12] for the elementary dipole moment one obtains $\mu \simeq 0.61\times 10^{-29}$ cm, which is too large to be attributed only to the deuteron in the hydrogen bond. The heavy-ion contribution to the elementary dipole moment is approximately 50%.

The value obtained for $J_{\perp}$ does not agree very well with the one from static dielectric data[8] ($J_{\perp}=0.83$ K), but it is closer to the one from neutron scattering analysis[12] ($J_{\perp}=2.1$ K). $J_{\perp}$ seems to be very much sample dependent and very sensitive to the degree of deuteration of the crystal.

The activation energy $\Delta U=450$ K $=0.039$ eV is very close to the corresponding value in KD_2PO_4,[21] indicating that the O—H(2) · · · O bonds in DCDP are very much the same as the hydrogen bonds in KD_2PO_4, as can also be concluded from the approximate equality of the bond lengths,[4,13] and of the deuteron quadrupole coupling constants[11] in these two systems.

The relaxation frequency of the noninteracting dipoles [Eq. (6)] at T_c equals 1.3×10^{13} s^{-1} and the corresponding relaxation time τ has the value of 1.2×10^{-14} s, which is 2 orders of magnitude smaller than the free-dipole relaxation time in KD_2PO_4. The KD_2PO_4 free-dipole relaxation time obtained by NMR (Ref. 23) equals 1.8×10^{-12} s, while its value obtained from dielectric data[21] using Eq. (8) is 1.6×10^{-12} s. The nonequality of the free-dipole relaxation times in these two systems can be understood in the following way. While the DCDP analysis in one-dimensional regime is exact, in the KD_2PO_4 studies the mean-field approximation is used [Eq. (8)], neglecting strong correlations between four deuterons around a given PO_4 group, which can be treated rigorously in the four-cluster approximation.[24] In a first approximation, mean-field results can still be used if one ascribes the two states $S^z=\pm 1$ to the two lowest energy states of the whole PO_4 group. The obtained relaxation time therefore describes the dynamics of the whole PO_4 group and is expected to be much larger than the relaxation time corresponding to a single hydrogen bond.

The value for τ obtained in a recent NMR analysis[11] in DCDP disagrees with our results by 2 orders of magnitude and is of the same order as the one in KD_2PO_4. This discrepancy seems to be a consequence of the fact that a much too small anisotropy ratio $J_{\parallel}/J_{\perp}=100$ was used in the analysis of the NMR data. Furthermore, only the critical region close to T_c was studied, where the linear-chain approximation [Eq. (10)] is not valid.

IV. CONCLUSIONS

Analysis of the dielectric relaxation in pseudo-one-dimensional ferroelectric CsD_2PO_4 in the vicinity of T_c shows classical Curie-Weiss behavior for the static dielectric constant, and nonclassical critical temperature dependence of the dielectric relaxation frequency with a critical exponent 1.3.

The linear-chain approximation, in which the interchain correlations are neglected, well describes the static and dynamic dielectric properties of the system outside the critical region ($T > T_c + 7$ K). The kinetic coefficient in this region is strongly temperature dependent because of one-dimensional intrachain correlations. Close to T_c an additional slowing down and a decrease of the kinetic coefficient (Fig. 5) are observed as a consequence of three-dimensional interchain correlations.

The intrachain and interchain interactions obtained agree well with previously determined values. The noninteracting deuteron intrabond relaxation time is much smaller than in KD_2PO_4, but has the same activation energy. It can be concluded that the double-well potential for a deuteron in a hydrogen bond is approximately the same in CsD_2PO_4 and in KD_2PO_4. To compare the properties of the two systems quantitatively the four-cluster analysis for dynamics in KD_2PO_4 is needed.

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