Comment on "Origin of low-frequency dielectric dispersion in KH_2PO_4 and RbH_2PO_4 ferroelectric crystals"

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Kim and Kim [Phys. Rev. B **59**, 13 509 (1999)] have studied the frequency dependence of the complex permittivity of KH_2PO_4 and RbH_2PO_4 in the ferroelectric phase. In the low-frequency regime ($f<10$ kHz) they found a dispersion consisting of at least three distinctive components. Considering the temperature dependence of those relaxational modes they claim that each of them is associated with domain wall motion, and not with a heat diffusion central peak (HDCP). The aim of this Comment is twofold: First we want to demonstrate the importance and influence of the ac measuring field on the dielectric properties, in particular in the temperature range $T<T_f=100$ K$<T_c$ of domain freezing. Second, by investigating the dielectric nonlinearity in the limit of small ac fields we exclude HDCP contributions in the low-frequency part of the spectrum.

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Recently the low-frequency properties of various materials have gained new interest[1–5] and have been interpreted as being due either to a heat diffusion central peak (HDCP) or to domain wall motion (DWM). In the case of elastic measurements a possible contribution of heat diffusion and DWM, respectively, can be separated conveniently: in a certain geometry contributions of DWM to the compliance are not allowed and the anomalous part in the compliance stems from heat diffusion. This has been discovered in several substances.[2,6] Moreover, the $\boldsymbol{q}$ dependence (thickness dependence) of the HDCP has been examined carefully. The resulting characteristic frequency followed a q^2 law which could be used as a definite proof that one is dealing with the heat diffusion. This method, being a fingerprint of the phenomenon, has not been employed in the previous dielectric studies.[1,3,4,7] Unlike in the elastic investigations, the problem arises in the dielectric measurement that the contributions of heat diffusion and DWM to the susceptibility cannot be separated by choosing an appropriate geometry. However, at least three methods can be used to distinguish between dielectric HDCP and DWM contributions:

(1) To measure the dielectric susceptibility on a monodomain sample.

(2) To examine the q dependence of the characteristic relaxation frequency by varying the thickness.

(3) To look for the temperature dependence of the characteristic relaxation frequency.

The first method is the best one from the theoretical point of view: Measuring on a monodomain sample a contribution due to DWM can be ruled out. A lack of dispersion in that case would mean that heat diffusion does not play any role. On the other hand, to induce the monodomain state in a KH_2PO_4 sample, a rather high electric dc-bias field is necessary which is difficult to apply in a low-frequency spectroscopical setup. Solving the problem by using method (2) similar to the elastic measurements is rather tempting. In ferroelectric multidomain samples, however, the domain structure, the number of domains and their dielectric response, is related to the thickness of the crystal.[8] Hence the results may be ambiguous, too. Kim and Kim[4] have chosen attempt (3). This is an indirect method as it makes assumptions on the temperature dependence of the thermal diffusivity. We acknowledge their efforts on contributing to the solution of the problem. However, as shown further the comparison of spectra taken at different temperatures requires the careful analysis of the influence of the temperature-dependent nonlinearity of KH_2PO_4.

In this Comment we lay emphasis on the importance and the influence of the measuring ac electric field on the dielectric susceptibility of KH_2PO_4 in the ferroelectric regime and demonstrate that the low-frequency dispersion is codetermined by that parameter. It will be shown that the ac electric field dependence observed in the dielectric spectrum of KH_2PO_4 renders it possible to exclude that the HDCP is responsible for the dispersion observed in the low-frequency range. Furthermore, we present measurements for KH_2PO_4 at various temperatures ($T<T_c$), frequencies (100 mHz–10 kHz), and ac measuring fields (10^{-2}–10 V/cm) on a thick ($t=4.37$ mm) sample. Similar investigations in studying DWM previously done by Malek *et al.*[9] for RbH_2PO_4 and Bornarel[10] for KH_2PO_4 in the early 1970s had been restricted to the range of higher frequencies.

Our sample was cut from a large highly purified crystal of KH_2PO_4 and has been described and characterized as a part of the sample S2 elsewhere.[11] The faces perpendicular to the ferroelectric c axis have been covered by evaporated silver electrodes. In view of the size of the KDP crystal available and the minimum ac voltage $U_{min}=0.004$ V applicable in our experimental setup, a rather thick sample with dimensions $5.85\times5.42\times4.37$ mm^3 was prepared for the dielectric investigations. For the highly purified (and thus highly nonlinear) crystal examined, this turned out to be a necessary condition to access the ac field range of the linear dielectric response in which the permittivity is independent of the ac

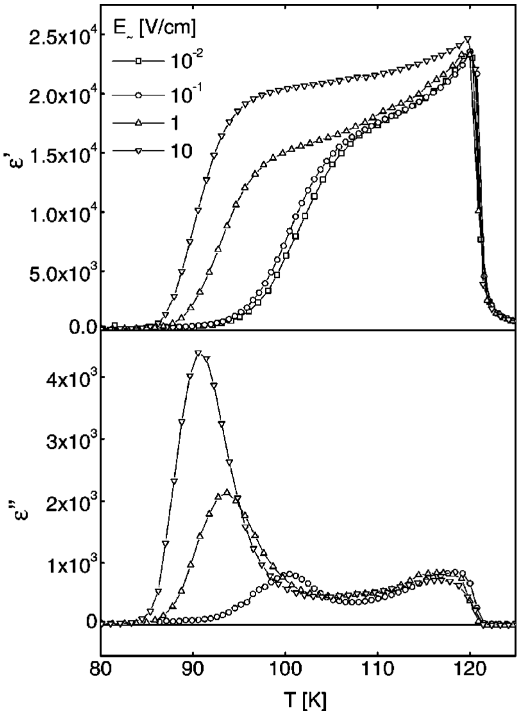

FIG. 1. Real ϵ' and imaginary ϵ'' parts of the dielectric constant in KH_2PO_4 as a function of temperature for a frequency of $f=1$ Hz and various ac measuring fields: $E_\sim=0.01$ V/cm, 0.1 V/cm, 1 V/cm, 10 V/cm.

field amplitude. The geometry of our sample which is rather unusual for dielectric experiments requires the careful analysis of the influence of the fringe field. This was established investigating a thin sample with nearly the same surface area and a thickness of 0.6 mm for which we obtained qualitatively the same results but could not eliminate the influence of the dielectric nonlinearity completely. The temperature of the sample has been controlled in an Oxford CF-cryostat with a stability better than ± 0.02 K. Using a DSP lock-in amplifier (SR850), we determined the complex permittivity as described in Ref. 4 from the voltage signal drop across a standard capacitor in series connection with the sample. We performed three different types of runs: temperature scans, ac electric field scans, and frequency scans where in each case the remaining two parameters were kept constant. In Fig. 1 we show the temperature dependencies of the real and imaginary parts of the dielectric constant in KH_2PO_4 for a frequency of $f=1$ Hz and various ac measuring fields covering three orders of magnitude. The cooling rate was 0.5 K/min. From Fig. 1 the tremendous influence of the ac measuring field can be clearly seen. Within the plateau region the influence of the ac field amplitude both on ϵ' and ϵ'' is obvious for $E_\sim \approx 1$ V/cm. Even more important, it becomes evident that the nonlinearity of KH_2PO_4 depends significantly on temperature. Within the freezing range $T<105$ K, we observe a dramatically increased nonlinearity leading to a width of the ϵ' -plateau range increasing with $E_\sim$. At the same time, the higher ac fields $E_\sim$ result in a strongly enhanced low-temperature freezing peak of the ϵ'' curve which is shifted towards lower temperatures. Clearly,

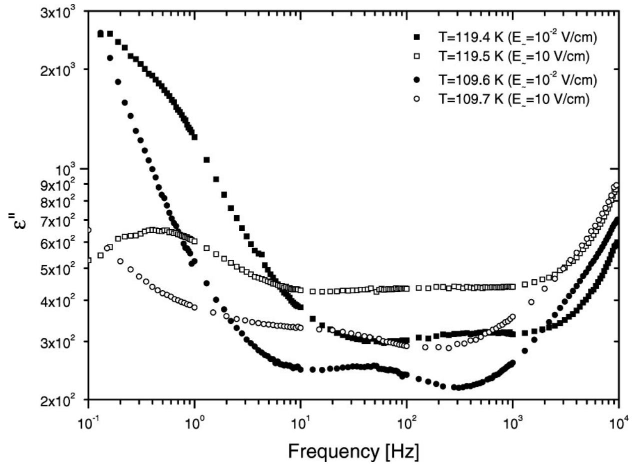

FIG. 2. Frequency dependence of ϵ'' for $T=119.5$ K (squares), $T=109.6$ K (circles) and $E_\sim=0.01$ V/cm (solid), $E_\sim=10$ V/cm (open), respectively.

changes of the ac field lead to far more distinct changes as compared to the frequency parameter which was considered in Ref. 4. Therefore, we conclude that the magnitude of the measuring field must be chosen very carefully not to work in a strongly nonlinear regime, in particular if low frequencies and the domain freezing phenomenon are considered.

Comparing our data obtained in the linear regime to the equivalent data of Ref. 4 it is striking that $\epsilon'(f\approx 1$ Hz, $E_\sim \approx 1$ V/cm) is almost one order of magnitude lower for the sample used in their investigation. This indicates that the quality of crystals varies from one group to another. The influence of crystal quality on the dielectric properties is known to be crucial in a lot of dielectrics, e.g., Rb_2ZnCl_4, TGS, and KH_2PO_4.[12–15] In general, the nonlinearity of the domain wall response is expected to decrease with increasing defect concentration. Thus the data obtained in Ref. 4 at a much higher ac field level as compared to those in the present study, nevertheless may correspond to the range of linear dielectric response. On the other hand, neither the sample dimension nor the crystal quality was specified in Refs. 1 and 3. Therefore, a direct comparison with our data cannot be obtained.

To support the importance of the ac field on the results, Fig. 2 gives the frequency dependence $\epsilon''(\omega)$ of the imaginary part of the complex permittivity for two excitation fields at two temperatures in the ferroelectric phase. Again, the decisive role of the exciting field both on the height and on the maximum frequency of the $\epsilon''(\omega)$ low-frequency peak is obvious. This result cannot be understood in terms of the HDCP contribution to the low-frequency dispersion in KH_2PO_4. Thus the analysis of the ac field dependence of the low-frequency dispersion represents an easy method to distinguish between HDCP and DWM contributions.

Finally, we give an additional argument concerning the heat diffusion central peak: Taking into account the thickness $t>4$ mm of our sample, the characteristic frequency of the HDCP dispersion should be expected at frequencies much lower than the frequency window investigated. From this point of view, the experiments in this study employ technique (2) in the limit of very large q values. Thus we can exclude that the various components of the dispersion at frequencies 100 mHz$<f<$10 kHz are related to the HDCP contribution, which is in agreement with the ac field dependence of the dielectric spectrum discussed above and the conclusion drawn by the authors of Ref. 4.

In conclusion, the low-frequency dispersion in KH_2PO_4 is uniquely related to the response of domain walls, which in turn is strongly determined by defects constituting the real structure of the crystal.

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