PROC. JSSF-2, KYOTO, 1980
J. PHYS. SOC. JPN. **49** (1980) SUPPL. B, pp. 188–190.

Investigation of Ferroelectric Excitations in Hydrogen-Bond Crystals Using the Method of Submillimeter Spectroscopy

G. V. KOZLOV, S. P. LEBEDEV, A. M. PROKHOROV and A. A. VOLKOV

P. N. Lebedev Physical Institute, Academy of Sciences of the USSR, Leninsky prospect 53, Moscow 117333, USSR

On the basis of the submillimeter dielectric spectra, the dispersion parameters of low-frequency lattice excitations in TGS, RS, ADP and DADP crystals were obtained. The relation between our results and previous data are discussed. We dwell on the question of critical absorption of electromagnetic radiation in KDP at phase transition point too.

The present paper is concerned with an investigation of dielectric spectra of hydrogen-containing ferroelectrics TGS, Rochelle salt, and KDP-type crystals in the 3–30 cm^{-1} frequency range. The aim of the investigation is to enlarge the experimental material on dynamic properties of these classic ferroelectrics which lack data concerning long-wave lattice excitations. The investigation has been carried out for all the crystals by a common scheme and consisted of measuring the frequency dependences of the real and imaginary parts ε' and ε'' of dielectric permeability in a wide temperature range using a laboratory submillimeter spectrometer.[1] The data on ε' and ε'' were then treated on the basis of simple phenomenological models for the purpose of establishing the parameters of the absorption spectral lines responsible for submillimeter dielectric dispersion.

KDP-type crystals

The results of our investigation of KDP, KDA, RDP and mixed KDP-DKDP crystals are summarized in ref. 2. Here we present some new information on antiferroelectric ADP and DADP and dwell on the question of critical absorption of electromagnetic radiation in KDP in the vicinity of the phase transition temperature.

Treatment of the obtained dielectric spectra of ADP and DADP has shown that:

1). In ADP dielectric dispersion at $E \parallel c$ is associated with the relaxation absorption line, and at $E \perp c$ with a strong damping but under damped one. Thus, the character of dielectric dispersion in ADP is the same as in KDP but mode at $E \perp c$ is a more intensive and lower-frequency as compared to $E \parallel c$. Neither of the modes considered has critical temperature dependence in ADP (Fig. 1).

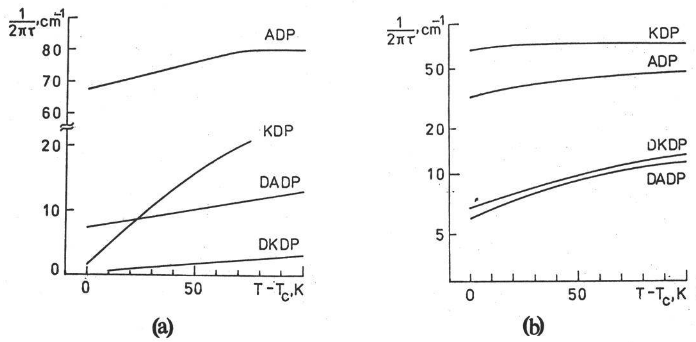

Fig. 1. Characteristic frequencies of proton modes of KDP type crystals
a) $E \parallel c$
b) $E \perp c$

2). In DADP characteristic frequencies of the modes decrease almost by an order, as compared to ADP, and both of them are purely relaxational excitations. The relationship of intensities and frequencies of modes $E \| c$ and $E \perp c$ are approximately the same in DADP and ADP.

A radical decreasing of the mode frequencies at deuteration indicates that these modes are directly associated with the proton (deutron) excitation on hydrogen bonds.

The change in the ratio of frequencies and intensities of the modes $E \| c$ and $E \perp c$ at transition from the ferroelectric KDP and DKDP to antiferroelectric ADP and DADP crystals is in agreement with Slater's concept on the sign reversal of the proton interaction energy ε_0 for a given type of substitution of atoms in the KDP crystals.[3]

The resonant character of $E \perp c$ mode in ADP indicates that despite the increasing of the proton potential energy on bonds in ADP (in comparison with KDP), the tunneling in the proton subsystem is preserved, and for description of the dynamic properties of ADP, it is necessary to develop a model considering in full extent the kinetic energy of protons. As to the properties of DADP crystals, the tentative results of our calculations have shown that they are well described in the framework of the existing claster models.

Proceeding to the second question, let us note that in this case we imply only a very particular effect observed in a series of works and pertaining so far to an actual problem of critical phenomena in ferroelectrics.

The effect consists of the fact that at frequencies of about 1–10 cm^{-1} the temperature dependences $\varepsilon''(T)$ of the KDP crystal for $E \perp c$ orientation manifest a sharp peak in the phase transition point (~ 1 K).[4] The latter was interpreted as an indicator of the losses increasing in the crystals due to the critical phenomena.[5]

Our experiments carried out at the temperatures close to the phase transition point, have shown that effect considered is caused rather by purely methodical reasons than the physical mechanism.

The essence is as follows. Very steep temperature dependences of the KDP dielectric properties at the phase transition point in the presence of any small temperature gradients make a sample dielectrically inhomogeneous. As a result the sample transmission coefficient decreases, that has been mistakenly interpreted as an increase in the value of ε''.

Our data on $\varepsilon^*(\nu, T)$ of the TGS crystal have been obtained for a high-frequency slope of a wide absorption line which causes ferroelectric dispersion. This line has been repeatedly investigated by the methods of radio-frequency measurements.[6-8] An attempt to describe our results in common with the lower-frequency data[8] on the basis of a simple relaxation model has shown that the dielectric dispersion observed at the submillimeter waves is too considerable and cannot be interpreted simply as a tail of some low-frequency mechanism. A transition to the model with the distributed relaxation time[6] does not result in a radical improvement of the description of dielectric spectra in all the frequency range from 10^{10} to 10^{12} Hz. At the same time the submillimeter data itself turned out to be in good agreement with the Debye model. This fact was a ground for using a model of two coupled relaxators for the treatment of dielectric spectra. The analysis has shown that in all the dispersion region this model gives the best agreement of the calculated and experimental data, as compared to all the models so far proposed. The obtained temperature dependences of the model parameters are shown in Fig. 2. According to the model there is a higher-frequency mode in TGS existing side by side with the well known intensive low-frequency excitation. It is advisable to have the detailed low-frequency data on ε' and ε'' in the temperature interval expanded into the high-temperature region for a more reliable

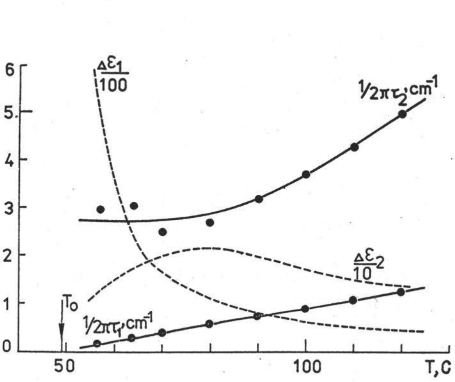

Fig. 2. Temperature dependences of the characteristic frequencies and dielectric contributions of relaxation excitations in TGS crystal.

confirmation of applicability of this model to the description of dielectric dispersion in TGS.

Rochelle salt

The treatment of the data $\varepsilon^*(\nu, T)$ obtained in the submillimeter wave region confirmed the relaxation character of the dispersion mechanism in RS established earlier on the basis of radiofrequency measurements.[9] In the temperature range 180–230 K, where the dispersion characteristic frequency is close to the operating frequencies, we managed to fit the relaxator parameters unambiguously without any assumptions on τ, $\Delta\varepsilon$, and ε_∞. The characteristic frequency of the ferroelectric excitation in RS becomes considerably lower the submillimeter region at 230–255 K, and ambiguity appears in the choice of the model parameters. To remove it we introduced the following condition into the treatment program

$$\varepsilon = \Delta\varepsilon + \varepsilon_\infty$$

where ε is the static value of ε'. This condition holds automatically in the temperature range 180–230 K.

The resulting dependence of the characteristic frequency of the mode $\nu \sim \frac{1}{\tau}$ is shown in Fig. 3. At the temperatures close to the point of phase transition $T = 255$ K, the values $1/2\pi\tau$ turned out to be close to those calculated in ref. 9. This apparently makes it possible to conclude that the dispersion observed in the submillimeter spectra is caused by the same relaxation phenomena which manifest themselves in the microwave and radio-frequency ranges. Some doubt about this conclusion is caused only by the pointed ambiguity in the choice of τ and $\Delta\varepsilon$ which, strictly speaking, does not exclude the probability that in RS like in TGS, two low-frequency modes exist in the vicinity of the transition point. But there is no direct indicators to this fact in the dielectric spectra.

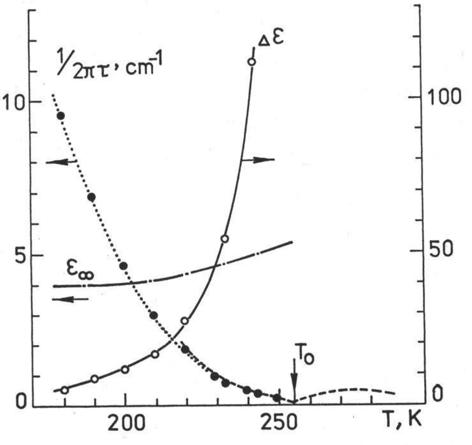

Fig. 3. Parameters of the ferroelectric relaxation mechanism in RS crystal.

The temperature behaviour of the characteristic frequency of the excitation discussed is seen to be rather unusual for ferroelectrics. The value $1/2\pi\tau$ increases very sharply with the descreasing temperature in the interval 180–250 K and can be approximated by the cubic dependence:

$$1/2\pi\tau = 1.07(275 - T)^3 \cdot 10^{-5}\ \mathrm{cm}^{-1}$$

Such a nonlinear dependence of the characteristic frequency of ferroelectric excitation was quantitatively described in the framework of the microscopic model of phase transition in RS.[10]

In conclusion the authors express their gratitude to N. A. Irisova, L. P. Levanyuk, R. R. Levitsky and L. A. Shuvalov for useful discussion of results.

References

1) A. A. Volkov, G. V. Kozlov and S. P. Lebedev: J. Teoreticheskoi i Eksperimentalnoi Fiziki, **79** (1980) 1430.
2) A. A. Volkov, G. V. Kozlov, S. P. Lebedev and A. M. Prokhorov: Ferroelectrics **25** (1980) 531.
3) Y. Ishibashi, S. Ohya and Y. Takagi: J. Phys. Soc. Jpn. **33** (1972) 1545.
4) K. E. Gauss, H. Happ and G. Rother: Phys. Status Solidi (b) **72** (1975) 623.
5) S. Havlin and H. Sompolinsky: Phys. Lett. **57A** (1976) 171.
6) R. M. Hill and S. K. Ichiki: Phys. Rev. **128** (1962) 1140; **132** (1962) 1603.
7) Yu. M. Poplavko, L. P. Pereverzeva, V. V. Meriakri, E. F. Ushatkin, S. V. Ogurtsov and P. I. Yaschishin: Fizika Tverd. Tela **15** (1973) 1250.
8) G. Luther: Phys. Status Solidi. (a) **20** (1973) 227.
9) F. Sandy and R. V. Jones: Phys. Rev. **168** (1968) 481.
10) R. R. Levitsky, I. R. Zackek and V. I. Varanitsky: Ukr. Fiz. J. **25** (1980) 000.