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# Resonance dielectric dispersion of TEA-CoCl₂Br₂ nanocrystals incorporated into the PMMA matrix

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**Abstract**
The dielectric properties of TEA-CoCl₂Br₂ nanocrystals incorporated into the polymethylmethacrylate matrix within the frequency range of $3 \times 10^5$–$2.6 \times 10^9$ Hz in the temperature region of 90–300 K were investigated. The considerable difference in the dielectric spectra of the nanocomposite compared to those of the bulk crystal and the pure polymer matrix was observed. The dielectric dispersion of the composite material reveals a resonance type (resonance frequency was found to be near 1.3 GHz) and may be qualitatively explained as the result of piezoelectric resonance on the nanocrystals. The model interpretation of this phenomenon based on the forced-dumped oscillator is presented.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Numerous crystals containing alkylammonium cations and inorganic anions are under detailed investigation by a large number of scientists due to the complicated sequences of different type phase transitions (PT), including transitions into the incommensurate phase, connected with dynamics of the organic cations and inorganic anions. Unfortunately, their technical application is restrained because of high hygroscopicity, brittleness and damage caused by overheating above 100 °C.

It was shown [1, 2] that incorporation of nanocrystals (NC) into a polymer matrix may open a new opportunity for application of semiconductor, oxide and dielectric NCs as materials for photo-operated nonlinear optics and photorefractive devices as well as for optically operated modulators, $Q$ switches, deflectors, etc. In order to explicate

such a possibility for alkylammonium tetrahalogenometallic compounds and, particularly, to investigate the influence of the quantum size effect on the physical properties and PTs of the mentioned solid solution polymer matrices with incorporated TEA-CoCl₂Br₂ ([N(C₂H₅)₄]₂CoCl₂Br₂) nanocrystals were prepared and their spectral and nonlinear optics properties were investigated [3–5].

According to [3] the bulk TEA-CoCl₂Br₂ crystal undergoes two structural phase transitions below room temperature—at $T_1 = 249$ K and $T_2 = 224$ K (on cooling). Also, it was suggested that below $T_2$ there exists the improper ferroelectric phase. On the basis of the spectral investigations performed it has been found that the temperature of phase transitions $T_2$ in the nanostructured ferroics could depend on a host polymer matrix and is higher than those in the bulk material [4]. Taking into account the supposed improper ferroelectric origin of the phase lying below $T_2$ it was

suggested that this effect is connected with the surface tension coupled with polarization via the electrostriction effect and influence of the depolarization field arising around the surface of the nanocrystal. As a result the improper ferroelectric phase is suppressed. Similar effects were predicted theoretically for ferroelectric nanotubes [6].

Moreover, it was found that the lateral pressure arising induces a lowering of the symmetry of the metal–halogen complexes within the surface layer of the NC. Their distortion is followed by a more pronounced splitting of the degenerate energy levels due to the lower symmetry of the crystal field, which becomes more pronounced with reduction of the sizes of the NCs [4].

In this paper we demonstrate how the dielectric properties of a TEA-CoCl$_2$Br$_2$ solid solution within the frequency range of $3 \times 10^5$–$2.6 \times 10^9$ Hz can be dramatically changed when the nanoparticles of this crystal are dispersed within the polymethylmethacrylate (PMMA) polymer matrix.

## 2. Experimental details

The samples of TEA-CoCl$_2$Br$_2$ were grown from aqueous solutions of N(C$_2$H$_5$)$_4$Cl, N(C$_2$H$_5$)$_4$Br, CoCl$_2$ and CoBr$_2$ salts taken in stoichiometric ratio. The synthesized samples were melted and crushed to grains within the 60–80 nm size range using an external acoustical focused field. The size dispersion was measured by a Brookhaven 90 nanoparticle size analyzer. From figure 1 one can see that most of the nanoparticles have sizes in the vicinity of 70 nm with some asymmetry of size dispersion.

Prepared NCs were first mixed with PMMA in the appropriate ratio and then dissolved in the chloroform solvent. The prepared solution was deposited on a round glass plate with a previously evaporated round gold electrode. After evaporation of the solvent the samples with 0.05–0.3 mm thickness and different concentrations of TEA-CoCl$_2$Br$_2$ NCs (3%, 5% and 7%) in the PMMA matrix were obtained.

The size distribution and uniformity of the TEA-CoCl$_2$Br$_2$ nanocrystals in the PMMA matrix were tested by SEM and TEM methods. The obtained size distribution of nanoparticles in the prepared samples shows good correlation with those presented in figure 1. The results of corresponding investigations will be published elsewhere.

The dielectric measurements within the frequency range of $3 \times 10^5$–$2.6 \times 10^9$ Hz were carried out using the vector network analyzer Agilent 8714ET with a BDS 2200 sample cell and BDS 2230 RF extension line. The samples were put into the sample cell with only an upper electrode. The influence of the electrode system (open and short) was accounted for. To exclude the geometry effects several nanocomposite disc-like samples with different thicknesses were prepared for measurement. Samples were placed between two sandwich electrodes, building a sample capacitor similar to the BDS 1200 cell. For reliability the electrode spacing was varied between 30 $\mu$m and 3 mm. In order to collect sufficient statistics each measurement was performed several times. The reproducibility of the data was better than 3.2%. So we believe, that all applied arrangements allowed us to
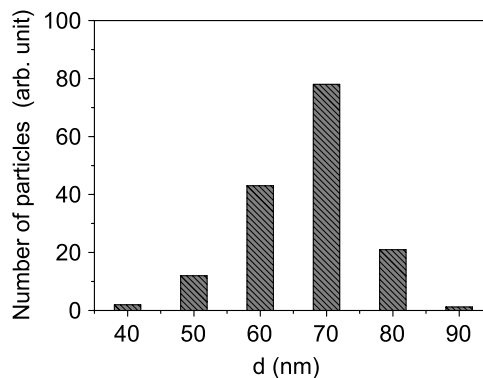


**Figure 1.** Size distribution of the nanoparticles.

enhance the precision of the measurements and to exclude both the existence of parasitic sample resonances and possible geometrical artifacts. The equations to calculate permittivity values and a detailed description of the experiment could be find in [7].

The x-ray diffraction data of the TEA-CoCl$_2$Br$_2$ powder sample were collected using an HZG-4A powder diffractometer (Cu K$\alpha$ radiation, $10° \geqslant 2\theta \geqslant 70°$ and step scan mode with a step size of $0.02°$). The crystal structure refinements were determined using the CSD program package [8].

The second harmonic generation (SHG) experiment was similar to [9] and was performed using the pulsed Nd:YAG laser ($\lambda = 1064$ nm, $\tau = 10$ ns) with 10 Hz frequency repetition and pulse peak power of 1 MW. As a reference sample we have utilized the KTiPO$_4$ NC incorporated into the same PMMA matrix at the same content.

## 3. Results

The dielectric properties of the pure PMMA were investigated fairly well [10, 11]. No significant frequency dispersion was detected by us within the $3 \times 10^5$–$2.6 \times 10^9$ Hz frequency range neither for pure PMMA nor for the bulk TEA-CoCl$_2$Br$_2$ crystal (see figure 2).

Both compounds demonstrate the flat frequency dependence of both the real and imaginary parts of $\varepsilon$. However, the frequency dispersion of the dielectric permittivity of the combined TEA-CoCl$_2$Br$_2$ NC–PMMA matrix material differs drastically from those obtained for pure compounds. As is seen from figure 3, there is a clearly pronounced resonance frequency dispersion of both the real and imaginary parts of the dielectric permittivity. We tested the composite compounds with three different concentrations of nanoparticles (3, 5 and 7%). The resonance frequency was found to be near 1.3 GHz and does not depend on NC concentration. However, the increase of the TEA-CoCl$_2$Br$_2$ NC concentration results in an increase of the resonance values of both $\varepsilon'$ and $\varepsilon''$. For the highest NC concentration (7%) the real part of the permittivity demonstrates the negative values within a certain frequency range above the resonance.

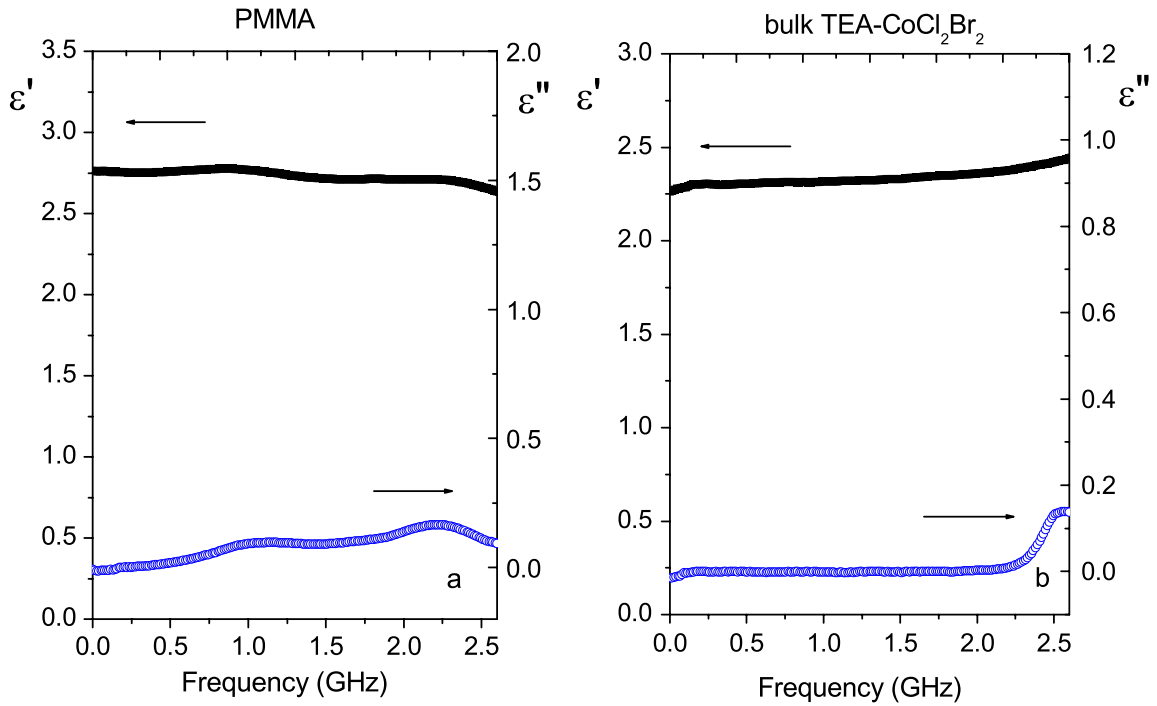It is worth noting that the dielectric resonance observed by us has no relation to the dimensional resonance effect

**Figure 2.** Frequency dependences of the real $\varepsilon'$ and imaginary $\varepsilon''$ parts of the dielectric permittivity for pure PMMA (a) and for bulk TEA-CoCl$_2$Br$_2$ (b) obtained at $T = 293$ K.
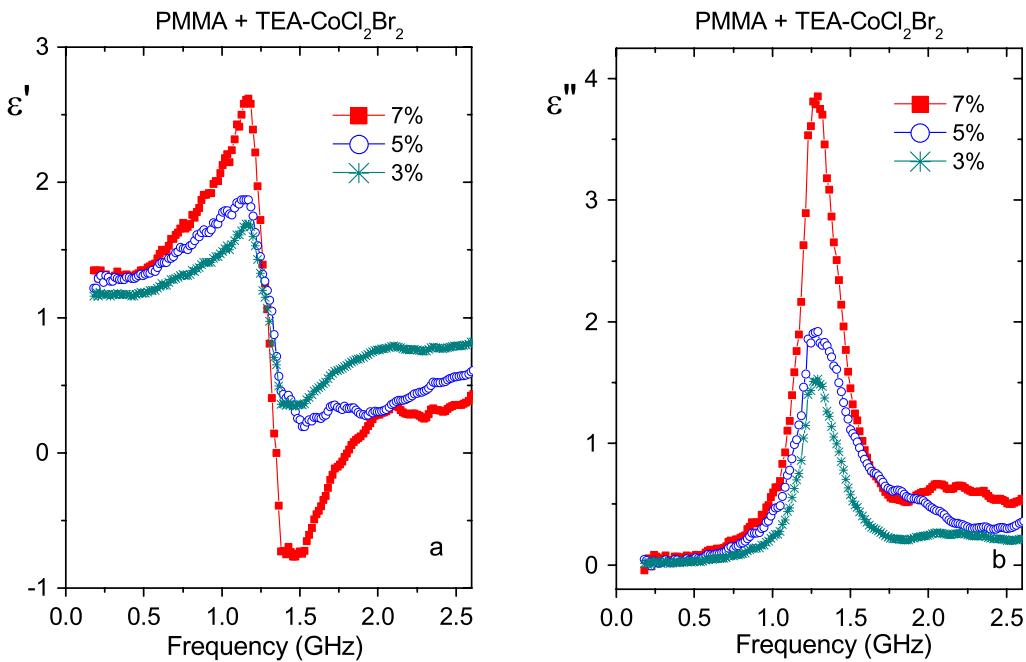


**Figure 3.** The real (a) and imaginary (b) parts of the dielectric permittivity as a function of frequency for PMMA + TEA-CoCl$_2$Br$_2$ with NCs concentration of 3%, 5% and 7% measured at room temperature.

connected with a macroscopic sample thickness [12]. In order to prove this we have performed the experiment with samples of different thicknesses. The obtained results (figure 4) show that the sample thickness at constant NC concentration does not influence either resonance frequency or resonance value of $\varepsilon'$. Therefore one can conclude that this phenomenon

is connected with the substantial physical properties of the material and not with its geometry.

In order to gain more information about the physical mechanism of this phenomenon, investigations of the dielectric permittivity were carried out for various temperatures and the results are plotted in figure 5 (for legibility the number
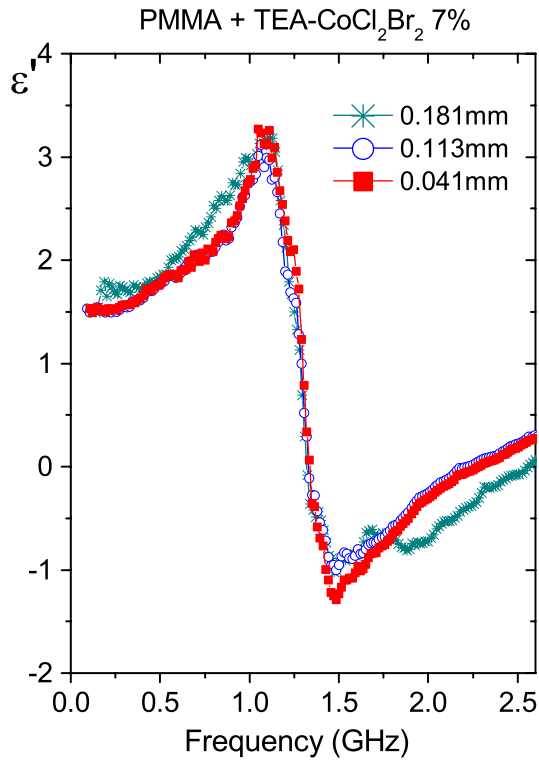
**Figure 4.** Frequency dispersion of the real part of the dielectric permittivity for PMMA + TEA-CoCl$_2$Br$_2$ samples at various thicknesses (at room temperature).



**Figure 6.** X-ray powder diffraction patterns of the TEA-CoCl$_2$Br$_2$ crystal measured (upper line) at room temperature and calculated (lower line) using the CSD program.

of temperature dependences was limited to three temperature points). As one can see from this figure the resonance frequency decreases upon cooling. This is accompanied by the diminution of the resonance values of both $\varepsilon'$ and $\varepsilon''$.
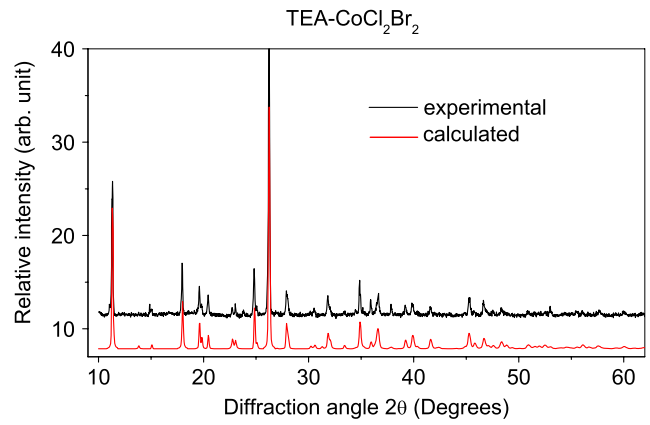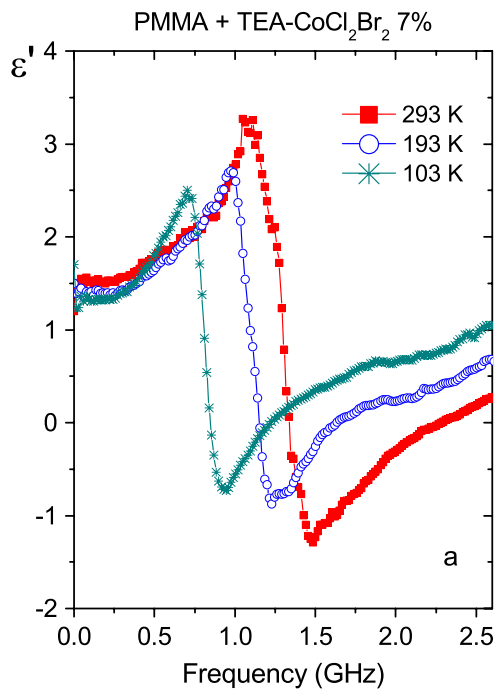
In order to test the presence of the structural acentricity in both the TEA-CoCl$_2$Br$_2$ compound and PMMA + TEA-CoCl$_2$Br$_2$ composite we have carried out a x-ray powder diffraction and SHG investigation, respectively. X-ray powder diffraction studies have revealed that the TEA-CoCl$_2$Br$_2$ is isomorphous with TEA-CoX$_4$ (X = Cl, Br) compounds, which belong to the $P4_2/nmc$ group of symmetry [13–15]. Experimental x-ray diffraction patterns of TEA-CoCl$_2$Br$_2$ powder and that simulated using the CSD program for $P4_2/nmc$ symmetry are shown in figure 6. We obtained a good agreement in peak position but some discrepancies in corresponding intensities. Such a result could be connected to the formation of a dominant texture ([001]) in the prepared powder sample. The unit cell parameters were found to be $a = b = 9.028(1)$ Å
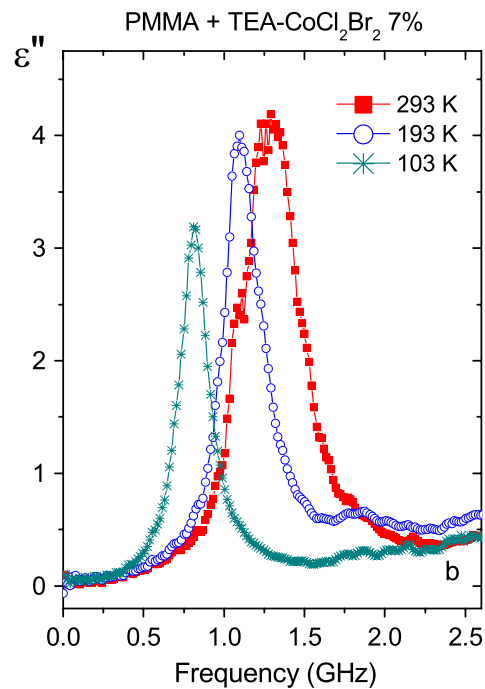


**Figure 5.** Frequency dependences of the real (a) and imaginary (b) parts of the dielectric permittivity for PMMA + TEA-CoCl$_2$Br$_2$ composite taken at various temperatures.

and $c = 15.404(2)$ Å. They are very close to those in TEA-$CoX_4$ (X = Cl, Br) crystals [13–15]. Therefore, one may infer that the centric $P4_2/nmc$ symmetry is relevant for the TEA-$CoCl_2Br_2$ crystal at room temperature.

The investigations of the SHG of composite material was performed at room temperature. We have found that the maximally achieved value of the effective second-order susceptibility was equal to about 0.56 pm V$^{-1}$. This value is certainly lower compared to the inorganic crystals like BBO (about 4.2 pm V$^{-1}$). However, it may be very critical that the reliable SHG signal exists in the investigated composites reflecting the existence of local acentricity in the investigated materials.

## 4. Discussion

Appearance of the negative dielectric permittivity is not an unusual phenomenon in solid state physics. The following relation [16]:

$$\varepsilon = \varepsilon_\infty \prod_j \frac{\omega^2 - \omega_{jLO}^2 - i\omega\gamma_a}{\omega^2 - \omega_{jTO}^2 - i\omega\gamma_a} \quad (1)$$

is generally used for description of the IR spectra in dielectrics. The dielectric permittivity manifests the negative value within the $\omega_{TO} < \omega < \omega_{LO}$ frequency region, where $\omega_{TO}$ and $\omega_{LO}$ are the transverse and longitudinal phonon mode frequencies, respectively. However, the typical frequency range where this phenomenon occurs lies in the far- and mid-infrared region ($10^{12}$–$10^{14}$ Hz).

Another phenomenon allowing the resonance frequency dependence of dielectric permittivity is the diffraction of the plane electromagnetic wave on the dielectric sphere placed within the medium with different dielectric permittivity [17]. Vendik *et al* [18] developed the theory suggested in [17] for the case of the medium composed from the three-dimensional lattice of dielectric spheres distributed in the dielectric matrix. According to [18], the effective permittivity $\varepsilon_{eff}$ function of such an artificial medium demonstrates the resonance frequency behavior with the negative values of $\varepsilon_{eff}$ above the resonant frequency:

$$\varepsilon_{eff}(\omega) = -\frac{4}{3} 2\pi \left(\frac{r}{s}\right)^3 \varepsilon_d$$

$$\times \frac{j_1(k_1r)N\left[k_1rh_1^{(1)}(k_1r)\right]' - h_1^{(1)}(k_1r)N\left[k_1rj_n(k_1r)\right]'}{N^2 j_1(Nk_1r)\left[k_1rh_1^{(1)}(k_1r)\right]' - h_1^{(1)}(k_1r)\left[Nk_1rj_n(k_1r)\right]'}, \quad (2)$$

where $j_1(z)$ and $h_1^{(1)}(z)$ are the spherical Bessel and Hankel functions, respectively, $r$ is the radius of the dielectric sphere, $k_1 = \omega\sqrt{\varepsilon_0\mu_0\varepsilon_d\mu_d}$, $N = \sqrt{\frac{\varepsilon_d\mu_d}{\varepsilon_m\mu_m}}$, $\varepsilon_d(\varepsilon_m)$ and $\mu_d(\mu_m)$ are the dielectric permittivity and magnetic permeability of the spherical particles (matrix), respectively, $s$ is the period of the artificial meta-lattice and $[\cdots]'$ implies the derivative with respect to $k_1r$ or $Nk_1r$.

The spherical diameter should be of the order of 1 mm in order for the resonance frequency to fall into the GHz region [18]. Wheeler *et al* [19] have shown that the three-dimensional lattice of micron-scale coated spheres demonstrates the resonance of both $\varepsilon_{eff}$ and $\mu_{eff}$ at infrared frequencies (THz region). Since in our case the NC size is dispersed within 60–80 nm, according to relation (2), $\varepsilon_{eff}$ must reach the enormous value of the order of $\sim 10^{12}$ to get the $f_r = 1.3$ GHz observed in our experiment. Despite the peak rise of dielectric permittivity up to $\sim 10^8$ observed in composite material formed from ferroelectric sodium nitrite nanoparticles in a porous opal matrix [20], we may not find the realistic physical mechanism allowing such a huge value of dielectric permittivity ($\sim 10^{12}$) in our TEA-$CoCl_2Br_2$ NC–PMMA material. Therefore, some other physical phenomenon should evoke the resonance of dielectric permittivity.

We believe that the reason for the observed dielectric anomaly may originate from the electromechanical piezoelectric resonance of TEA-$CoCl_2Br_2$ NCs. However, as follows from our x-ray data, the bulk TEA-$CoCl_2Br_2$ crystal manifests the centric $P4_2/nmc$ symmetry at room temperature and, hence, would not have piezoelectricity. On the other hand, composite PMMA + TEA-$CoCl_2Br_2$ material demonstrates the macroscopic acentricity which was clearly observed in our SHG experiment. It is obvious that the total acentricity of the composite compound may only be evoked by the acentric symmetry of TEA-$CoCl_2Br_2$ NC. Apparently, the PMMA matrix should reveal the electret properties [21] polarizing the NCs dispersed in it. Influence of the internal electret field of PMMA should play the key role in creating the acentricity in the TEA-$CoCl_2Br_2$ NCs as well as in the temperature shift of the resonance frequency. Some analogy could be made with the poling of piezoceramics. The resonance frequency depends on the value of the applied poling electric field [22]. Moreover, the additional investigation revealed the presence of the pyro-electric polarization in PMMA + TEA-$CoCl_2Br_2$ composites (corresponding results will be presented elsewhere).

It was shown [23, 22] that piezoelectric resonant spectra can be described by the model of multiple forced-dumped oscillator:

$$\varepsilon(\omega)^* = \varepsilon'(\omega) + i\varepsilon''(\omega) = \varepsilon_c + \sum A_i \frac{(\omega^2 - \omega_{0i}^2) - i2\gamma_i\omega}{(\omega^2 - \omega_{0i}^2)^2 + 4\gamma_i^2\omega^2}, \quad (3)$$

where $\omega_{0i}(d)$ and $A_i(d)$ are the dimension-dependent resonant (or characteristic) frequency and amplitude of the *i*th oscillator, respectively. $\gamma_i(d)$ and $\varepsilon_c(d)$ are the dumping factor and 'clamped' dielectric permittivity, respectively. In this model, positive and negative ionic units oscillate in opposite directions under the influence of an applied ac electric field. Such an approach is similar to that described by equation (1), but it gives a lower frequency due to the cooperative character of the considered effect. The dimensional dependence of the parameters in equation (3) occurs since the piezoelectric resonance is a macroscopic cooperative phenomenon in which the sample (NC) size, shape and boundary conditions play essential roles. The detailed theoretical description could be found in [23, 22, 24].

According to the structural data the oscillating charges in TEA-$CoCl_2Br_2$ can be the $[CoCl_2Br_2]^{2-}$ anion from one side and a couple of $[N(C_2H_5)]^+$ cations as the second part of
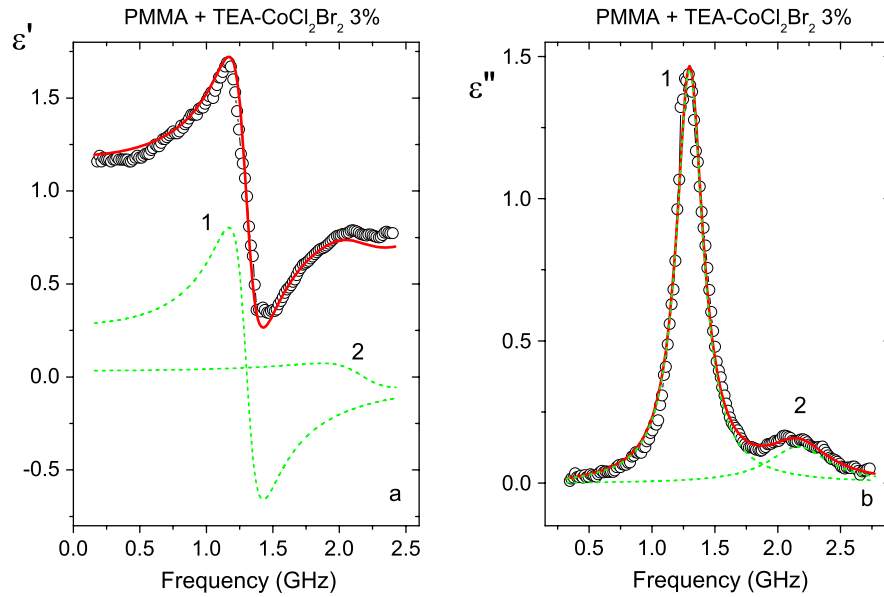
**Figure 7.** The results of approximation of the real (a) and imaginary (b) parts of the dielectric permittivity for PMMA + TEA-CoCl$_2$Br$_2$ with NCs concentration of 3% using equation (4). Peaks 1 and 2 are shown by the dotted lines. The solid line is the sum of fittings with $\varepsilon_c = 0.871$.

**Table 1.** Fitting parameters used for simulation of the resonance spectra of PMMA + TEA-CoCl$_2$Br$_2$ (3%).

| Peak | $\omega_0/2\pi$ (GHz) | $A/(2\pi)^2$ (GHz$^2$) | $\gamma/2\pi$ (GHz) |
|------|------|------|------|
| 1 | 1.305 | 0.487 | 0.129 |
| 2 | 2.181 | 0.161 | 0.2876 |

the oscillating unit. Such an assumption fairly well correlates with the results of the low frequency dielectric studies of TEA-CoCl$_2$Br$_2$ bulk crystal that revealed dispersion connected with cooperative motion of the oppositely charged complexes mentioned [25].

Using equation (3) we can approximate the experimental spectra (see figure 7). It was found that the high frequency tail of $\varepsilon''$ of TEA-CoCl$_2$Br$_2$ is similar to that for pure PMMA and, therefore, was subtracted. For the best fit it is necessary to take several resonance curves. Some discrepancy between the fitting curve and the experimental data of the real part of $\varepsilon$ in the high frequency region is connected with the contribution of the dielectric dispersion of the PMMA matrix which, in this case, could not be simply taken into account. Two different resonance curves may correspond to either thickness or radial extension mode. Although the designation of these modes concerns the macroscopic sample, their frequencies are determined by the corresponding sizes of the NCs. The parameters of approximation are presented in table 1. The considerable width of the resonance region is more likely connected with the dispersion of the sizes of the nanocrystals and their orientation in the sample.

On the other hand, it is generally accepted to treat the object of piezoelectric resonance around the resonant frequency as the electrical equivalent LCR circuit [26, 27]. The resonant frequency $f_r$ may be given as

$$f_r = \frac{1}{2\pi\sqrt{LC}} = \frac{1}{2d}\sqrt{\frac{C_{\text{eff}}}{\rho}}, \quad (4)$$

where $d$ is the average diameter of NCs, and $C_{\text{eff}}$ and $\rho = 1.45$ g cm$^{-3}$ are the effective elastic constant and the density of TEA-CoCl$_2$Br$_2$ NCs, respectively. As follows immediately from equation (4), $C_{\text{eff}}$ should be equal to $4.84 \times 10^7$ and $1.35 \times 10^8$ Pa in order to satisfy the experimentally observed values of resonant frequency $f_r = 1.3$ GHz and $f_r = 2.181$ GHz ($d$ was put as 70 nm). These values of $C_{\text{eff}}$ are two orders of magnitude smaller than those usually observed in other related ferroelectric bulk crystals (see, e.g., [28–31]). This discrepancy evidently is connected with the surface phenomena, such as a lateral (surface) tension characteristic of the nanostructured ferroics [4]. Therefore, the elastic properties should strongly depend on the size of NCs since the surface to volume ratio increases with the diminishing size of the NCs. The interface borders separating the nanoparticles and the polymer also modify considerably the elastic properties of the NCs [5]. The considered effects as well as the change of the poling electret field of the matrix cause a temperature shift of the resonance frequency.

## 5. Conclusions

Taking into account that no noticeable frequency dispersion was detected either for the TEA-CoCl$_2$Br$_2$ bulk crystal or for pure PMMA in the frequency region under investigation, the frequency dispersion of resonance type observed in the present work has to be treated as the physical phenomenon intrinsic to the composite material. The dielectric dispersion of the TEA-CoCl$_2$Br$_2$ NC–PMMA matrix compound reveals

the resonance frequency dependence of both $\varepsilon'$ and $\varepsilon''$ with resonant frequency near 1.3 GHz. The resonant frequency does not depend on the concentration of NCs in the host matrix, displaying at the same time the temperature shift to the lower frequencies upon cooling.

The principal experimental findings of the present work (occurrence of the resonance of dielectric permittivity, size independence of the resonance frequency and dependence of the resonance peak of $\varepsilon$ on NC concentration in the host matrix) may be explained as the result of the piezoelectric resonance of NCs. Since the bulk TEA-CoCl$_2$Br$_2$ crystal has the centric symmetry at room temperature, piezoelectricity in TEA-CoCl$_2$Br$_2$ NCs may only appear as a result of inverse symmetry violation within the electret PMMA matrix.

The observed phenomenon could find its application in the creation of high frequency piezoelectric transducers.

## Acknowledgment

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