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Dielectric Dispersion in Crystal $(NH_4)_2SO_4$

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The behavior of complex dielectric permittivity of the crystal $(NH_4)_2SO_4$ *was investigated in the frequency range of* $10^{-2} \div 10^9$ *Hz. The measurements of* ε^* *were conducted by bridge methods up to 1 MHz. At high frequencies the* ε^* *value was determined with the help of the coaxial reflector meter using the results of measurements of a reflection coefficient of the TEM wave in the coaxial line. In a ferroelectric phase the temperature dependence of dielectric permittivity is described by the Debye equation. The observed relaxation process is a representative of a typical relaxation polarization. The relaxation time of polarization computed on the base of experimental data for frequencies higher than 50 MHz is subjected to the Arrhenius equation. The mechanism of polarization concerning the observed behavior of* ε^* *is explained.*

Keywords Ammonium sulfate; ferroelectrics; dielectric dispersion; dielectric relaxation; phase transition

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Introduction

The crystal of ammonium sulphate (AS) with a formula of $(NH_4)_2SO_4$ at the $T_C = 223$ K undergoes a pseudo-proper phase transition (PT) from a paraelectric orthorhombic phase Pnam to a ferroelectric orthorhombic phase $Pna2_1$ with a doubling of a volume of an unit cell [1]. A behavior of AS, similar to the ferroelastic one, recently was revealed in the region of the ferroelectric PT. The crystal of AS in a phase (D_{2h}^{16}) has mechanical twins with planes of twinning (011) and (031) [2] and angles $\Theta = 58°48'$ for (011) twinning plane, $\Theta = 61°12'$ for (031) twinning plane. The presence of such ferroelastic twins in AS is explained by the existence of hexagonal praphase with symmetry D_{6h}^4 [3]. These ferroelastic domains can be switched from one orientation state to another by external stress. In related crystals K_2SO_4 and Rb_2SO_4 a phase transition from a rhombic phase to a hexagonal P63/mmc (D_{6h}^4) phase takes place at 560 K and 930 K accordingly. Earlier it was considered, that in AS such transition could not be realized because of melting above 400 K. However, the exotic behavior of AS recently was revealed in the range of 408–413 K [4, 5] at a temperature cycling of a crystal. The maiden heating of a crystal does not reveal any anomalies in this interval of temperatures. However, maiden cooling up to room temperature and the subsequent temperature cycling demonstrates the existence of anomalies in behaviors of real and imaginary parts of the dielectric permittivity at frequencies more than 500 Hz. As a frequency $\nu < 500$ Hz the anomalies of ε^* were not observed. The analysis of X-ray data [6] showed that in the temperature range of 413–423 K the anomalies in lattice parameters a, b,

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c are observed. The authors made a conclusion about the existence of PT in this temperature range, but the crystal has an orthorhombic space group Pnam from room temperature up to 463 K.

The study of dielectric permittivity of AS at low frequencies of 100 Hz–100 kHz has shown decreasing of ε from 220 up to 70 [7–10]. For explanation of the behavior of ε near the PT some models were proposed. In particular, it was supposed, that the observed ε behavior is related to the existence of two nonequivalent dipoles of ammonium NH_4 (I) and NH_4 (II), one of them becomes antiparallel directed one below T_C as a result of the order—disorder PT. The other mechanism was offered also, in which PT in AS is considered as PT that produced by distortions arising in sublattice of SO_4 ions and resulted in the greater degree in modifying the structure and symmetry of ions, than their positions and orientations in a crystal.

In the present paper the behavior of complex dielectric permittivity ε^* was investigated in the frequency range of $10^{-2} \div 10^9$ Hz. The measurements were conducted by bridge methods up to 1 MHz. At large frequencies ε^* was gauged with the help of the coaxial reflector by results of measurement of a reflection coefficient of the TEM wave in a coaxial line loaded with a cylindrical sample, arranged at the end of a line between the conductive insert and the short-circuit cylinder piston.

1. Measuring Technique

The measurements of complex dielectric permittivity were conducted in a broad frequency range from 10^{-2} to 10^8 Hz for finding a picture of dielectric anomalies and critical phenomena accompanying them, as well as for obtaining dielectric spectra and a type of dispersion (relaxation or resonance) near PT.

The measurements at frequencies of $10^{-2} \div 10^3$ Hz were conducted by the determination of a current through a measuring cell with the ferroelectric and ferroelastic sample under study, the components of which are proportional to real ε' and imaginary ε'' parts of complex dielectric permittivity. The generator of input sine-wave signals of an infra-low frequency was constructed on a base of a DAP producing a signal, the frequency of which was changed by the computer program.

The block-diagram of the device extracting complex values A(t) and B(t) from a mixture of a signal and a noise is shown in Fig. 1. In the range of frequencies 10^2–10^5 Hz the measurements were conducted by bridge methods with the help of standard devices "TESLA VM-507, R-571, R-568, E8-2, and E7-9. At frequencies of 1–10 MHz the phase meter F235 was used. For all listed devices the interface schemes were designed permitting to conduct

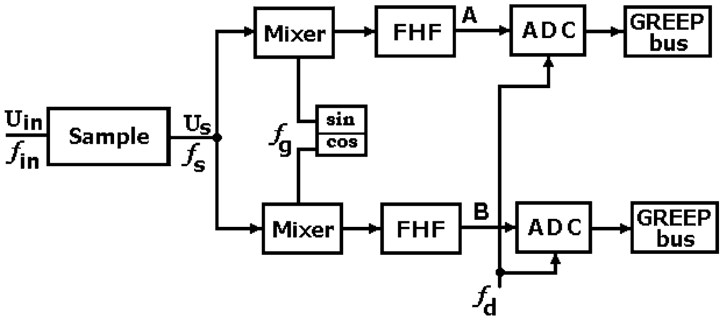

FIGURE 1 Block-diagram for measurement of complex dielectric permittivity at low frequencies.

measurements at intermediate frequencies at any definite temperature. They enabled us studying a behavior of ε^* in one sample and to increase a reliability of obtained data.

In a frequency range of 10^{-3}–10^{7} Hz the sample had a form of a plate with 1mm thick and area of surface up to 10 mm^2. Silver electrodes were deposited in vacuum using a three electrode scheme with protective ring. The cell with a sample was hooked up to measuring bridges with the 4-wire scheme.

In a frequency range of 0.2–1 GHz the complex dielectric permittivity was determined with the help of the coaxial reflectometer, by a measurement of a reflection coefficient $R(\nu,T)$ of TEM wave in a coaxial line loaded with a cylindrical sample of 0.4 mms in length and radius 1.8 mms, placed at the end of a line between a conductive insert and short piston. The admittance of the sample was determined using a reflection coefficient $R^* = |R| \exp(i)$ and capacitance of the sample C_s in accordance to [11]:

$$Y_s = \frac{1}{Z_o}\frac{1 - R^*}{1 + R^*} = i\varpi(C_s^* - C_a), \tag{1}$$

twhere Z_o is the wave line resistance, C_a is a parasitic capacitance introduced by an edge effect, and measured experimentally. If the dielectric loss are not great and the condition of quasi-stationarity is satisfied

$$r \le \frac{0,24\lambda}{2\pi\sqrt{\varepsilon}}, \quad d \le \frac{\lambda}{2\sqrt{\varepsilon}}, \tag{2}$$

then the dielectric permittivity is determined from (1) in accordance with formula of static condenser; if the conditions (2) is dissatisfied, dielectric permittivity determines in accordance with formula of dynamic condenser, taking into account a nonhomogeneous distribution of an electrical field in the sample.

The reflection coefficient was measured with usage of the scheme of the reflectometer shown in Fig. 2. The incident and reflected signals amplified by the frequency converter were detected with synchronic amplitude and phase detectors. The output of a phase detector has a voltage that is proportional to a phase shift between both signals.

2. Experimental Results and Discussion

The temperature dependences of ε' and ε'' for different frequencies of a measuring field are shown in Fig. 3. The maximum of dielectric permittivity ε' shifts to higher temperature with increase of a measuring field frequency, and its value decreases. It indicates a connection

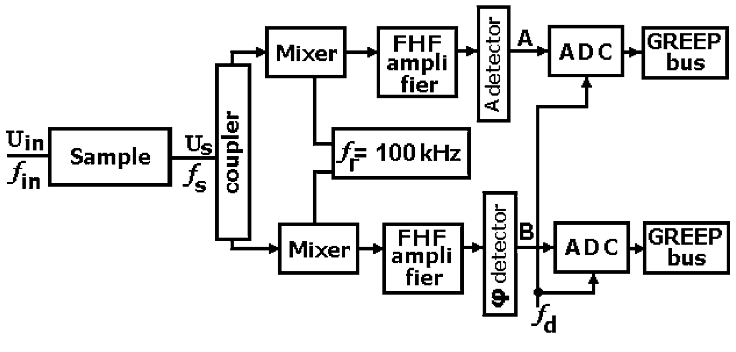

FIGURE 2 Block-diagram of the coaxial reflectometer set-up.

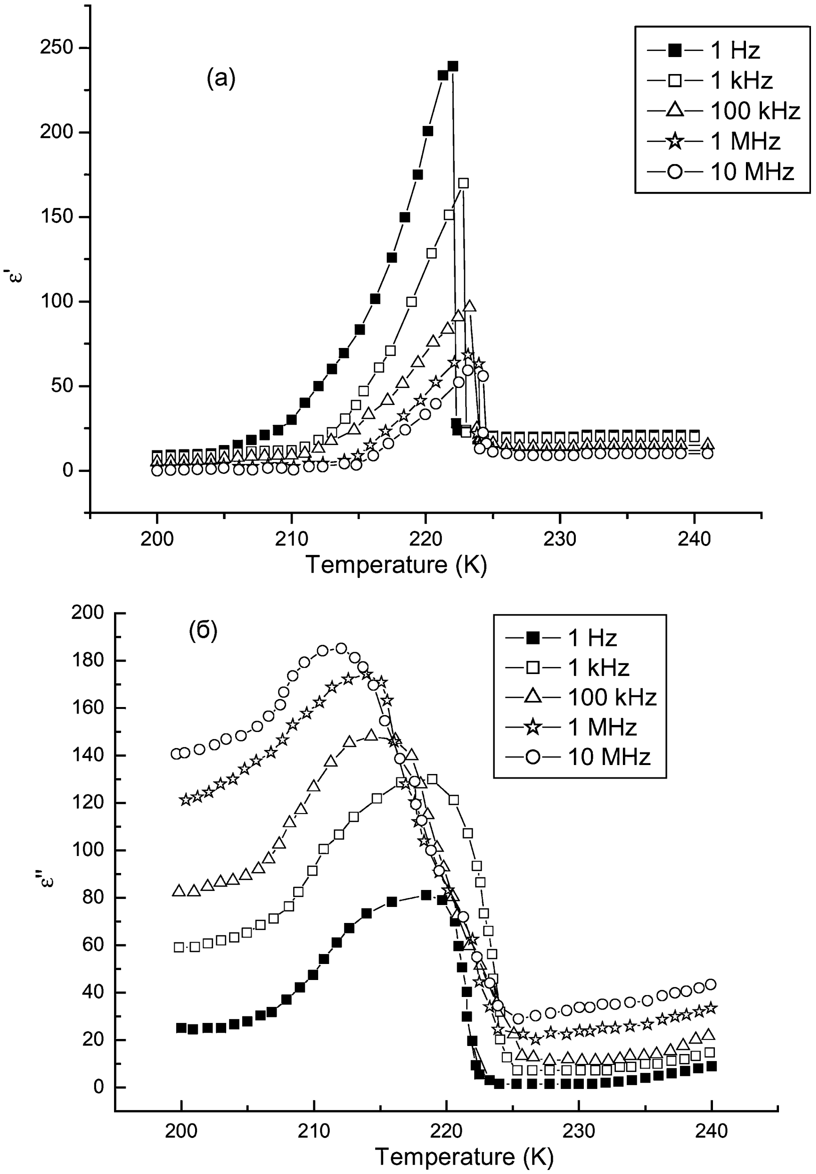

FIGURE 3 Temperature dependences of (a) real and (b) imaginary parts of the dielectric permittivity along c-axis at various frequencies.

of ε with relaxation polarization processes. In a ferroelectric phase and near to a transition point the temperature dependences of dielectric permittivity are described by the Debye equation for relaxation polarization

$$\varepsilon^*(\nu, \mathrm{T}) = \varepsilon_\infty + \frac{\varepsilon_\mathrm{s} - \varepsilon_\infty}{1 + \mathrm{i}\varpi\tau}. \tag{3}$$

Here ε_s and ε_∞ are accordingly low and high frequency limits of a dispersion region, τ is the relaxation time.

The temperature dependences of ε'' are displayed in Fig. 3(b), in which one can see that ε'' reaches its maximum value just below the Curie point. Taking the extremums in the

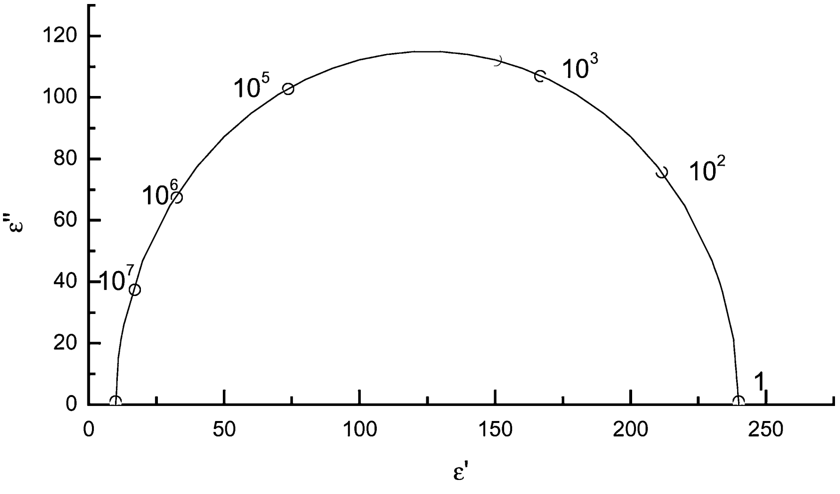

FIGURE 4 The Cole-Cole plot for the ammonium sulfate near the phase transition temperature. The points are the experimental data at T = 223.25 K. Frequencies of a measuring field are indicated in Hz). A line is a calculation by the Debye equation.

frequency and temperature dependences of ε'', the temperature relation of the relaxation time was calculated.

In Fig. 4 the Cole-Cole plot for AS is shown at a temperature of the ferroelectric phase (T = 223.5 K). It is seen that the dispersion of ε^* in investigated frequency range in a polar phase is predominantly of Debye type. The figures near points in Fig. 4 indicate frequencies of a measuring field in hertz.

The Fig. 5 demonstrates a frequency dependence of a real part of permittivity near T_C. In the range of frequencies 10^3–10^5 Hz a Debye type relaxation of domain walls occurs.

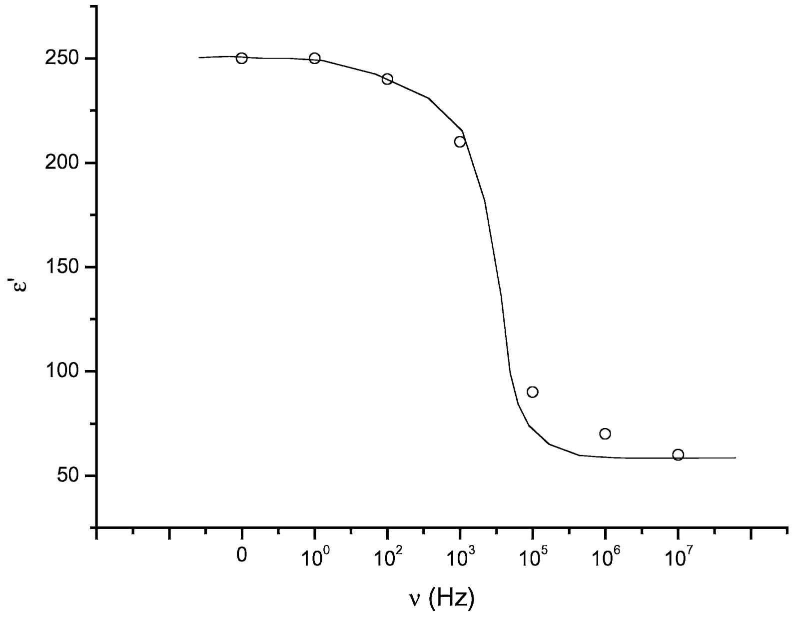

FIGURE 5 Frequency dependence of real part of the dielectric permittivity at T_C.

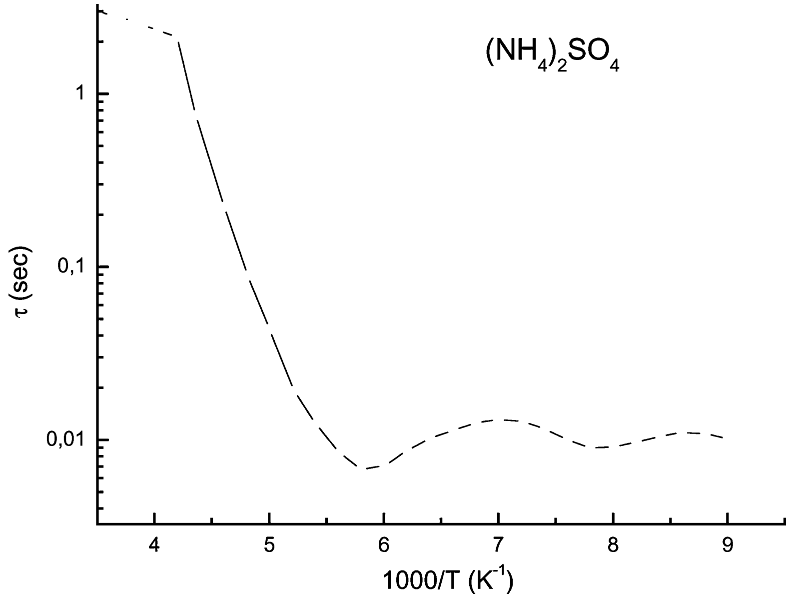

FIGURE 6 Temperature dependence of relaxation time.

Temperature dependence of a relaxation time is shown in Fig. 6. One can see that τ decreases sharply at the temperature of PT. The relaxation time computed on the base of experimental data for ε is obeyed the Arrhenius equation

$$\tau = \tau_0 \exp(\Delta U/kT). \tag{4}$$

Concerning the nature of the found relaxation processes it is possible to suppose, that they are connected with the distortions of AS crystal lattice at the PT temperature. This supposition is confirmed by the data [12, 13], according to which there are strong bonds between SO_4^{2-}—$NH_4^+(\alpha)$ and SO_4^{2-}—$NH_4^+(\beta)$ in AS. The displacement and the tilt of $NH_4^+(\alpha)$ tetrahedrons at the T_C occur together with $NH_4^+(\beta)$ tetrahedrons. These changes should be connected with deformation of a tetrahedron SO_4^{2-} and change the nature of bonds, as the electric charge transfers from NH_4^+ to SO_4^{2-}. The formation of electrical dipole moment in SO_4^{2-} leads to essential increase in energy of the exchange dipole-dipole interaction, as a distance between dipoles is considerably decreased. The energy of the dipole-dipole interaction for a system of tetrahedrons of ammonium and sulfate ions is essentially increased near the phase transition temperature, while the components of electrical dipole moment, directed along the c-axis, change insignificantly. The main driving force for the transition is concentrated around SO_4^{2-} ions. The NH_4^+ ions simply follow the change that is forced in them. Rotations of tetrahedral ions do not create a structure that can have a ferroelectricity unless the ions are distorted. The distortion is the prerequisite condition for the coupling between the rotation of ions and polarization of the crystal.

The study conducted in this work and also analysis of the references testify that a dispersion spectrum and the dynamic properties of AS have a number of features. At first, near the PT the considerable dielectric anomalies are seen, which essentially differ from corresponding behavior of ε^* in ferroelectrics of the displacement type or order-disorder type. Namely, the dielectric permittivity obeys the Curie-Weiss law in a very narrow temperature range and has a small value of the Curie constant. Besides the dielectric permittivity in the ordered phase measured on heating tends to be less, than on cooling, probably, because of irreversible motion of domains [7].

Secondly, the development of a soft long-wave optical phonon mode in AS, accountable for transition in the far infrared [14, 15] and low-frequency Raman [14] spectra down to 30 cm^{-1} phonon frequency was not revealed. The libration mode of tetrahedral ions is forbidden both in IR and Raman spectra. Consequently, the mode of SO_4^{2-} ions having almost tetrahedral structure in paraelectric phase of AS can not give the observable intensity. Even in the ferroelectric phase it can give only a low intensity.

And, at last, the dispersion of ε^* is observed in AS in broad frequency and temperature ranges. It has relaxation nature both in high and low regions. The dielectric spectrum has an intricate shape because of the contributions of several different mechanisms.

Thus, relaxation processes related to distortions in frame of SO_4^{2-} tetrahedrons influence on dielectric properties of the AS crystal. These processes result in strong frequency and temperature dependences of ε^* and tgδ.

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