RELAXATION AND RESONANCE ACOUSTIC ANOMALIES IN SOLIDS WITH HIGH IONIC CONDUCTIVITY AS STUDIES BY ACOUSTO-OPTICS

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Abstract

Review of studies of acoustic anomalies in solids with high ionic mobility (superionic crystals and glasses, crystals with high-temperature impurity and vacancy conductivity) using the Bragg light diffraction by ultrasound is presented. Relaxation sound attenuation arising due to various kinds of acousto-ionic interaction in piezoelectric and nonpiezoelectric materials is considered. It is shown that activation enthalpies, relaxation times, and attempt frequencies can be found from measurements as well as the ionic Maxwell's frequency in piezoelectrics. The newly observed phenomenon of temperature-dependent resonance ultrasound attenuation in the $LiIO_3$ and mixed CeF_3 crystals is discussed. The phenomenological theory of resonance acoustic anomalies near the superionic phase transition is suggested. Experimental data obtained show that the acousto-optical method provides a powerful probe of ionic conductivity in solids.

Introduction

Along with various technical applications, acousto-optical methods are used in physical acoustics. Their advantages compared to conventional ultrasonic techniques consist in extremely large frequency range up to several GHz, high sensitivity, and in possibility to measure the absolute values of sound attenuation. The most widespread acousto-optical method is based on Bragg diffraction of laser beam by ultrasonic wave. This method was shown to be especially fruitful for studies of solid ionic conductors. In the present paper we consider two kinds of acoustic anomalies related with high ionic mobility in crystals and glasses: relaxation anomalies, which nature is similar to relaxation alterations in electric conductivity and susceptibility, and newly observed resonance phenomena.

Relaxation acousto-ionic interaction

Relaxation anomalies for piezoelectrically active acoustic waves in piezoelectric crystals arise because of interaction of electric fields induced by sound with the mobile ions. The treatment of these effects is based on the modified Hutson-White-theory taking into account the delocalized as well as localized ionic movement. According to the theory, the sound propagation is described by the complex elastic modulus which leads to the following expression for the attenuation coefficient [1,2]:

$$\alpha=(K^2/2\upsilon_0)(\omega^2/\omega_c)/(1+(\omega/\omega_c)^2), \qquad (1)$$

where K is the electromechanical coefficient, ω is the ultrasound frequency, $\omega_c=\sigma/\varepsilon\varepsilon_0$ is the Maxwell frequency of conductivity relaxation, $\varepsilon=\varepsilon'-i\varepsilon''$, σ is the conductivity which includes ionic transport σ_c and the polarization contribution $\sigma_p=\varepsilon_0\varepsilon''\omega$. The latter is caused by localized ionic jumps. For crystals, the Debye model with one relaxation time τ and activation enthalpy H is often valid. Then

$$\varepsilon'=\varepsilon_c-\delta\varepsilon\omega^2\tau^2/(1+\omega^2\tau^2),$$
$$\varepsilon''=\delta\varepsilon\omega\tau/(1+\omega^2\tau^2),\ \delta\varepsilon=\varepsilon_c-\varepsilon_\infty, \qquad (2)$$

and

$$\tau=\exp(H/k_BT)/(2\nu), \qquad (3)$$

where ν is the effective attempt frequency of ionic jumps, ε_∞ and ε_c are high and low-frequency conductivity corresponding to $\omega\tau>>1$ and $\omega\tau<<1$. The conductivity σ_c is given by

$$\sigma_c=(nq^2a^2\nu'/bk_BT)\exp(-H'/k_BT), \qquad (4)$$

where n and q are number and charge of mobile ions, a is the jump length, H′ and ν' are activation enthalpy and attempt frequency for the delocalized ion movement, b is the numerical factor which depends on dimensionality of ionic mobility. For solid electrolytes ($\delta\varepsilon=0$) maximum of sound attenuation should be observed at $\omega=\omega_c$. For localized ions, the relationship (1) can be written as

$$\alpha=(K^2/2\upsilon_0)(\omega\varepsilon'/\varepsilon')/(1+(\varepsilon'/\varepsilon'')^2). \qquad (5)$$

The attenuation maximum should correspond to a temperature when $\omega\tau=\varepsilon_c/\varepsilon_\infty$.

It follows form (1) that for low sound frequency ($\omega<<\omega_c$) $\alpha=(K^2/2\upsilon_0)(\omega^2/\omega_c)$, while for high frequency ($\omega>>\omega_c$) $\alpha=(K^2/2\upsilon_0)\omega_c$, that corresponds to frequency independent sound attenuation.

For nonpiezoelectrically active acoustic modes in piezoelectric crystals, for nonpiezoelectric crystals and glasses, the sound attenuation is mainly caused by local relaxation processes [1]. This effect is referred to as relaxation due to deformation potential interaction. In this case the attenuation coefficient is given by

$$\alpha=(nB^2/2\rho v_0^3 k_B T)(\omega^2\tau/(1+\omega^2\tau^2)), \quad (6)$$

where B is the deformation potential. The relaxation time τ corresponds to ionic jumps between equilibrium positions and is given by (3). It follows from (6) that attenuation maximum should be seen upon the condition $\omega\tau=1$. As for piezoelectrically active waves, the attenuation coefficient has different frequency dependences in low and high-frequency limits.

We have studied relaxation acousto-ionic interaction using the acousto-optical method in several solids with high ionic mobility: superionic glasses with lithium conductivity, pure superionic $LiKSO_4$ and $Li_2B_4O_7$ crystals, $LiIO_3$ crystals with high localized mobility grown upon various conditions, doped and pure $Li_2Ge_7O_{15}$ crystals with high ionic mobility at elevated temperatures, doped $PbMoO_4$ crystals with mobile impurity ions, $LiNbO_3$ crystals with various stoichiometry influenced the high-temperature ion mobility [1-8].

For instance, the strong acousto-ionic interaction was observed in the $Li_2B_4O_7$ crystal for the piezoelectrically active acoustic wave travelling along the z axis contrary to weak sound attenuation for the acoustic wave travelling along the x axis (Fig.1). This agreed with the one-dimensional ionic conductivity in $Li_2B_4O_7$. The activation enthalpy and deformation potential were evaluated. Temperature and frequency dependences of ultrasound attenuation could be quite well described with the Hutson-White-theory taking into account only the delocalized ionic mobility.

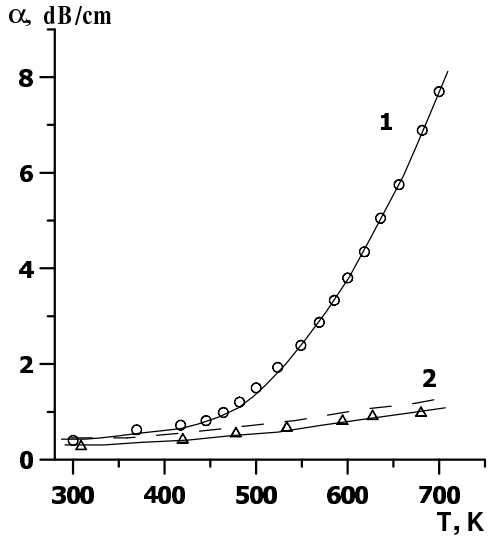

Figure 1. Temperature dependences of the ultrasound attenuation coefficient in the $Li_2B_4O_7$ crystal for the piezoelectrically active wave propagated along the z axis (1) and the nonpiezoelectrically active wave propagated along the x axis (2) at 400 MHz. The dotted line shows the Akhiezer contribution to attenuation of the piezoelectrically active wave.

Acousto-ionic interaction in the $LiIO_3$ crystals grown from solution with various pH was studied in [2,4,5]. Temperature and frequency dependences of sound attenuation for longitudinal and transverse ultrasound waves propagated along different crystal axes were observed (Fig.2). The quasione-dimensional ionic mobility was evidenced. The remarkable influence of the pH value on ionic mobility was revealed. The experimental results were treated within the framework of the modified Hutson-White theory and the deformation potential model for piezoelectrically active and nonpiezoelectrically active waves, respectively.

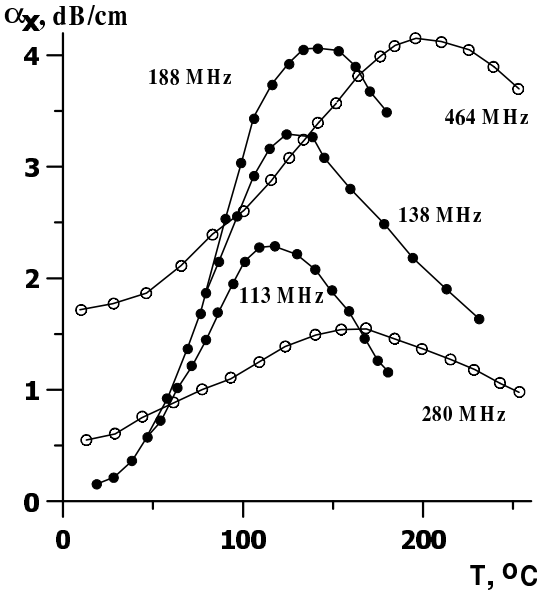

Figure 2. Temperature dependences of ultrasound attenuation for piezoelectrically active longitudinal wave (open symbols) and nonpiezoelectrically active transverse waves (closed symboles) propagated along the x axis for the LiIO3 crystal grown from solution with pH=0.8 at several frequencies.

Resonance ultrasound attenuation near the diffuse superionic phase transition

Until now it was commonly accepted that relaxation alterations as were discussed above are the only effect of ionic mobility on acoustic properties. However, it was observed recently [9,10] in two crystalline materials with high ionic mobility some special resonance sound attenuation, peaks of which shifting to higher temperature with increasing sound frequency. Temperature dependences of sound attenuation for the aluminum doped CeF_3 and $LiIO_3$ crystals are shown in Figs.3 for CeF_3. To prove the resonance nature of acoustic anomalies observed, the frequency dependences at various temperatures were also measured [10].

Since both the CeF_3 and $LiIO_3$ crystals have the diffuse superionic phase transitions (transitions occurring without lattice symmetry changes [11]) it was suggested in [9-10] that the resonance sound attenuation is related with those transitions.

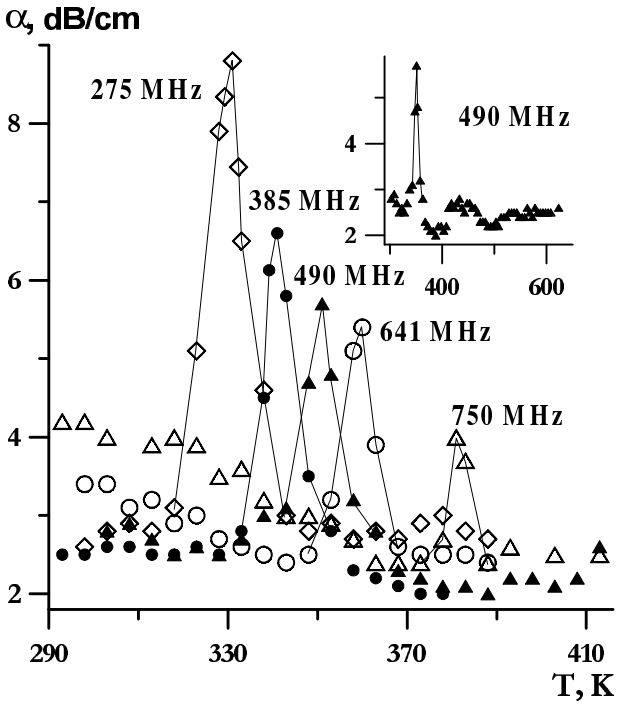

Figure 3. Ultrasound attenuation coefficient α versus temperature in the CeF_3 crystal for various frequencies. The inset shows the α versus temperature dependence for 490 MHz. Solid lines are guides for the eye.

To treat the resonance acoustic behaviour we assume that the phase transition is described by the phenomenological order parameter η and occurs at some temperature T_c. The order parameter is coupled nonlinearly with the strain in the acoustic wave ε. The Landau expansion can be written as

$$\Phi = \Phi_o + \frac{1}{2}a\eta^2 + \frac{1}{4}b\eta^4 + \frac{1}{2}c\varepsilon^2 + \frac{1}{2}r\eta^2\varepsilon, \quad (7)$$

where $a=a_o(T_c-T)$; a_o, b, and r are phenomenological coefficients; c is the elastic modulus below T_c. Because of the coupling between the strain ε and the order parameter η, the latter can be written as $\eta = \eta_0 + \eta_1$, where η_o is the equilibrium order parameter in the absence of acoustic wave and η_1 depends on time and position. Combining the relationship (7) with the equation for the order parameter $m\ddot{\eta} + \Gamma\dot{\eta} = -\partial\Phi/\partial\eta$ (m and Γ are the effective mass and damping) and with the equation for the elastic stress $\sigma = \tilde{c}\varepsilon = \partial\Phi/\partial\varepsilon$ one can obtain the following expression for the attenuation coefficient for $T>T_c$:

$$\alpha = \frac{a_o r^2 (T - T_c)}{2bv^3\rho} \cdot \frac{\omega^2\Gamma}{m^2(\omega^2 - \omega_o^2)^2 + \omega^2\Gamma^2}, \quad (8)$$

where $\omega_o^2 \equiv -2a/m$, v is the ultrasound velocity and ρ is the crystal density. As expected, the relationship (8) describes the resonance ultrasound attenuation above T_c with maximums at frequencies $\omega=\omega_o$. Since ω_o^2 depends linearly on temperature according, the resonance maximums should shift to high temperature with increasing frequency of ultrasonic waves in agreement with Figs.3. It is also easy to see that there is the following relation between the ultrasound frequency f and temperature T_m of the attenuation peak at this frequency:

$$f^2 = a_o(T_m - T_c)/(2\pi^2 m). \quad (9)$$

The satisfaction of the relationship (9) can serve as a criterion for the validity of the above theoretical model. The experimental dependence of f^2 on T_m obtained from temperature and frequency dependences of sound attenuation for the CeF_3 crystal is shown in Fig.4. The points corresponding to expected positions of the attenuation peaks on the attenuation coefficient versus frequency plots are also marked by crosses. The f^2 versus T_m dependence can be approximated by a straight line, which crosses the abscissa axis at T_c according to (9). It follows from Fig.4 that $T_c \cong 325$ K. The estimate obtained for T_c agrees with the fact that no relevant attenuation

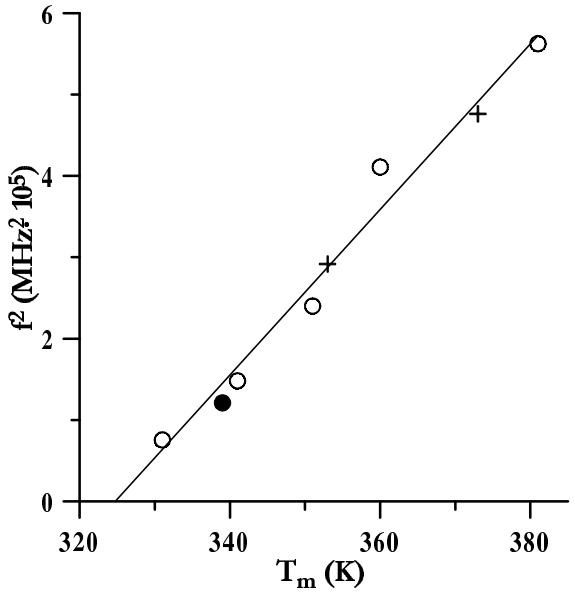

Figure 5. Squared ultrasound frequency versus temperature of attenuation maximum obtained from temperature (open circles) and frequency (closed circle and crosses) dependences of ultrasound attenuation in the doped CeF_3 crystal. Straight line is a result of least square fitting.

maximums were observed for temperatures 290 and 312 K which are below the phase transition assumed. The suggestion about the existence of the superionic phase transition at about 325 K agrees with measurements of electric conductance and NMR in the CeF_3 sample under study.

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