Resonance ultrasound attenuation in the doped CeF_3 superionic crystal

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Acousto-optical studies of temperature and frequency dependences of ultrasound attenuation in the doped CeF_3 crystal with high fluorine conductivity revealed resonance peaks that shifted to high temperature with increasing ultrasound frequency above room temperature. The temperatures of the attenuation maximums were found to depend linearly on the squared frequency of the ultrasonic waves. The resonance phenomena observed were treated within the framework of the Landau phenomenological theory under the assumption that a superionic phase transition occurs at about 325 K. The studies of electrical conductance and ^{19}F nuclear magnetic resonance were carried out to confirm such assumption.

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I. INTRODUCTION

Crystals and glasses with high ionic mobility show pronounced changes in temperature dependences of their acoustic properties due to the acoustoionic interaction (see Refs. 1–4, and references therein). For piezoelectric crystals and piezoelectrically active ultrasonic waves, the acoustoionic interaction is described by a modified Hutson-White theory (see Refs. 5 and 6, and references therein). For glasses, nonpiezoelectric crystals and nonpiezoelectrically active waves in piezoelectric crystals, the acoustoionic interaction is described within a theory of the deformation potential.[1,7] In this particular case, strong ultrasound attenuation is observed within temperature ranges where frequencies of ionic jumps are comparable with those of ultrasonic waves (see, for example, Refs. 1–3, 8–10). The theory of the deformation potential as well as the modified Hutson-White theory predicts the relaxation behavior of ultrasound attenuation and velocity. This provides a powerful probe of superionic conductors. Some studies were also devoted to acoustic properties in the vicinity of the superionic phase transition. Noticeable anomalies of elastic constants were observed near the superionic phase transitions for crystals in which the high ionic conductivity occurs following changes in the lattice symmetry.[12–15] The softening of the c_{44} modulus in $RbAg_4I_5$ provides an example of such kind of anomalies.[16] The character of alterations in elastic moduli in this case depends on coupling between acoustic modes and the order parameter. Temperature and frequency dependences of ultrasound attenuation through structural phase transitions to the superionic state can be described generally within the framework of relaxation dynamics similar to the sound wave relaxation near the ferroelectric phase transitions.[12] However, sometimes the attenuation peaks were observed above the transition temperatures,[17] the nature of those peaks was not clear. For diffuse superionic phase transitions, gradual changes in temperature dependences of elastic moduli were found in the vicinity of the transitions (see Ref. 18 and references therein).

Until now it was commonly accepted that such alterations as were discussed in Refs. 1–18 are the only effect of ionic mobility on acoustic properties. However, it will be shown below that one can also observe, in solids with high ionic mobility, some special resonance sound attenuation, peaks of attenuation shifting to higher temperature with increasing sound frequency. To show this, an acousto-optical technique was employed, which generally allows studying acoustic properties of transparent solids in a very wide frequency range from about 30 MHz to at least 1.5 GHz.[19–21] The most conventional acousto-optical method is based on Bragg diffraction of laser beam by ultrasonic wave.[20] This method is especially suitable to measure the frequency and temperature dependences of ultrasound attenuation in superionic crystals and glasses.[4,6,8,22] The measurements in the present paper were carried out for the superionic crystal $Ce_{0.95}Al_{0.05}F_3$ with fluorine conductivity. An assumption was made that the resonance sound attenuation occurs in the vicinity of a superionic phase transition and can be treated within the framework of the phenomenological Landau theory.

II. EXPERIMENT

The $Ce_{0.95}Al_{0.05}F_3$ single crystal was grown by the Bridgman-Stockbarger method. According to x-ray powder diffraction, the crystal structure is tysonitelike. The lattice parameters are $a=7.177$ Å and $c=7.277$ Å. The sample under study had a form of a parallelepiped with sizes of $14\times10\times6$ mm^3 cut along the crystallographic axes. Measurements of absolute values of sound attenuation for longitudinal waves were performed using Bragg diffraction of the Helium-Neon laser beam by ultrasound within the temperature range 290–625 K for ultrasound frequencies f from 128 to 932 MHz. Ultrasonic waves were generated along the x axis by means of $LiNbO_3$ plate transducers at odd harmonics. The $Y+36°$ cut plates were used with thickness of 200 μm and fundamental frequency of about 18.3 MHz. Transducers of such cut are known to generate mainly longitudinal ultrasonic waves. While slight admixture of transverse waves might be seen at some frequencies, the diffraction by longitudinal and transverse waves can be easily distinguished due to great difference in the Bragg angle. Measurements were performed upon slow warming from room temperature. The

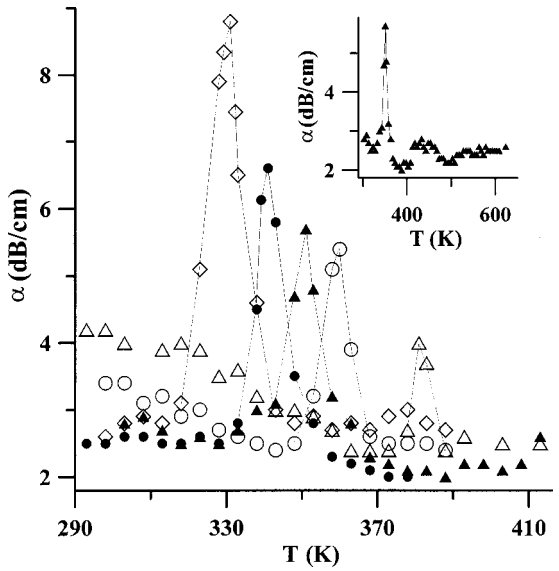

FIG. 1. Ultrasound attenuation coefficient α versus temperature for different frequencies: 275 (diamonds), 385 (closed circles), 490 (closed triangles), 641 (open circles), and 750 MHz (open triangles). The inset shows the α versus temperature dependence for 490 MHz. Solid lines are guides for the eye.

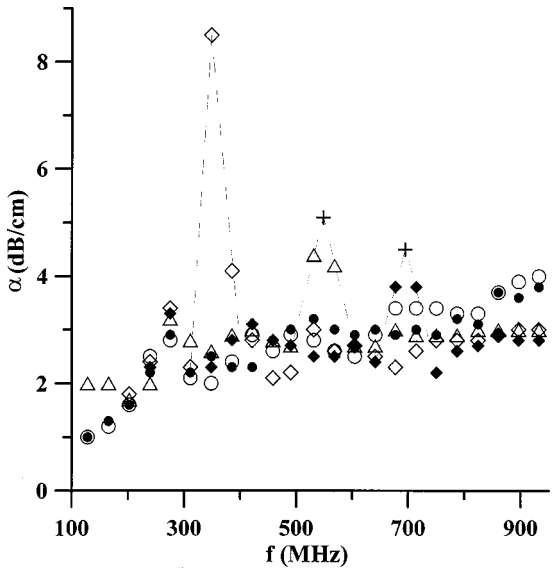

FIG. 2. Ultrasound attenuation coefficient α versus frequency for different temperatures: 290 (open circles), 312 (closed circles), 339 (open diamonds), 353 (triangles), and 373 K (closed diamonds). Dashed lines are guides for the eye. Crosses mark positions expected of attenuation peaks.

rate of change of temperature was no more than 1 deg/min. Prior to each measurement the sample was kept at a fixed temperature for about 10 min. The accuracy of temperature control was better than 1.5 K. Normally, to evaluate the ultrasound attenuation coefficient the intensity of the diffracted light beam was measured at 10 equidistant points along the direction of the ultrasound wave travelling. Thus, any measurement of attenuation at some particular temperature and frequency took about 30 min. Experimental accuracy of the attenuation coefficient measurements was about 10%. However, for attenuation less than 2.5 dB/cm, the results were influenced by some background attenuation discussed in Ref. 20.

The temperature dependences of the ultrasound attenuation coefficient for five different frequencies in the range from 275 to 750 MHz for the sample under study are shown in Fig. 1. One can see noticeable narrow peaks, which shift to higher temperature with increasing frequency. The intensity of the peaks in Fig. 1 decreases with increasing frequency; no distinct peaks could be distinguished for frequencies higher than 800 MHz. No visible anomalies in attenuation were observed above 400 K as can be seen from an example in the inset in Fig. 1. The shape of the peaks in Fig. 1 evidences clearly that their nature differs from relaxation ultrasonic attenuation that can be usually observed in the superionic phase since relaxation peaks for higher frequencies embrace generally those for lower frequencies. To confirm the resonance character of the peaks in Fig. 1, we performed measurements of frequency dependences of the attenuation coefficient at various temperatures. Some results are shown in Fig. 2. Distinct peaks of ultrasound attenuation can be seen at 339, 353, and 373 K; these peaks displace to higher frequencies with increasing temperature. Note that due to discrete resonance frequencies of the $LiNbO_3$ transducers, the measurements of frequency dependences are rather rough compared to those of the temperature dependences. Thus, frequencies corresponding to the attenuation maximums at 353 and 373 K can be only estimated according to expectations for the peak shape. The relevant positions of attenuation maximums in Fig. 2 are marked with crosses. For 290 and 312 K, the frequency dependences in Fig. 2 do not show any significant attenuation peaks that displace with the changing temperature. However, a weak but unambiguous peak is seen in Fig. 2 at 275 MHz for all temperatures used in the present study. The nature of this peak is not clear. Nevertheless, this peak being independent of temperature, one can speculate that it arises due to acoustic losses in the ultrasound section.

III. DISCUSSION

The temperature and frequency dependences shown in Figs. 1 and 2 reveal the resonance nature of the attenuation peaks observed. Until now, such resonance sound attenuation in superionic crystals was not observed. However, it is known that resonance phenomena at high frequencies can arise near phase transitions with oscillatory dynamics of the order parameter.[23] Thus, resonance phenomena observed for the crystal under study can be treated if one assumes that a phase transition, which is described by the phenomenological order parameter η, occurs at some temperature T_c. The order parameter should be equal to zero below T_c and should appear above T_c to explain acoustic anomalies at higher temperatures. Such a suggestion is normal for the superionic phase transitions.[1,12] The order parameter is coupled nonlinearly with the strain in the acoustic wave ε if the phase transition is implied not to be a proper or pseudoproper ferroelastic one.[24] When assuming a particular form of this cou-

pling, the Landau expansion can be written as

$$\Phi = \Phi_0 + \tfrac{1}{2} a \eta^2 + \tfrac{1}{4} b \eta^4 + \tfrac{1}{2} c \varepsilon^2 + \tfrac{1}{2} r \eta^2 \varepsilon, \quad (1)$$

where $a = a_0(T_c\text{-}T)$; a_0, b, and r are phenomenological coefficients; c is the elastic modulus below T_c. Due to the coupling between the strain ε and the order parameter η, the latter can be written as $\eta = \eta_0 + \eta_1$, where η_0 is the equilibrium order parameter in the absence of acoustic wave and η_1 depends on time and position. Combining the relationship (1) with the equation for the order parameter

$$m \ddot{\eta} + \Gamma \dot{\eta} = -\partial \Phi / \partial \eta, \quad (2)$$

where m and Γ are the effective mass and damping, one can obtain in linear approximation the following relation between η_1 and ε:

$$\eta_1 = \frac{r \eta_0}{m\omega^2 - i\omega\Gamma - a - 3b\eta_0^2} \varepsilon, \quad (3)$$

where $\omega = 2\pi f$. Substituting Eq. (3) into the equation for the elastic stress

$$\sigma = \tilde{c}\varepsilon = \partial \Phi / \partial \varepsilon, \quad (4)$$

retaining in Eq. (4) only terms associated with the acoustic strain, and using the relationship $\eta_0^2 = -a/b$ above T_c, one can obtain the following expression for the complex dynamic elastic modulus $\tilde{c}$:

$$\tilde{c} = c - \frac{ar^2}{b} \frac{1}{m(\omega^2 - \omega_0^2) - i\omega\Gamma} \quad (5)$$

for $T > T_c$ and $\tilde{c} = c$ below the phase transition temperature. Here

$$\omega_0^2 \equiv -2a/m. \quad (6)$$

From Eq. (5) on can deduce a relationship for the sound attenuation above the phase transition using the general equation $\alpha = (\omega/2vc)\mathrm{Im}\,\tilde{c}$, which is valid for weak attenuation,[20]

$$\alpha = \frac{a_0 r^2 (T - T_c)}{2bv^3\rho} \frac{\omega^2\Gamma}{m^2(\omega^2 - \omega_0^2)^2 + \omega^2\Gamma^2}, \quad (7)$$

where v is the ultrasound velocity and ρ is the crystal density. As expected, the relationship (7) describes the resonance ultrasound attenuation above T_c with maximums at frequencies $\omega = \omega_0$. Since ω_0^2 depends linearly on temperature according to Eq. (6), the resonance maximums should shift to high temperatures with increasing frequency of ultrasonic waves, in agreement with Figs. 1 and 2. The expressions (6) and (7) yield the following relation between the ultrasound frequency f and temperature T_m of the attenuation peak at this frequency:

$$f^2 = a_0(T_m - T_c)/(2\pi^2 m). \quad (8)$$

The satisfaction of the relationship (8) can serve as a criterion for the validity of the above theoretical model. The experimental dependence of f^2 on T_m obtained from Figs. 1 and 2 is shown in Fig. 3. The points corresponding to crosses in Fig. 2 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 Eq. (8). It follows from Fig. 3 that $T_c \cong 325$ K. The estimate obtained for T_c agrees with the fact that no relevant attenuation maximums were observed for temperatures 290 and 312 K (see Fig. 2), which are below the phase transition assumed. Note that the increase in attenuation at high frequencies near room temperature is most probably due to ordinary relaxation absorption induced by the acoustoionic interaction with maximum at lower temperatures. It should be also noted that the reduction in the peak intensity for high ultrasound frequencies, which is not predicted by the relationship (7), can be explained by the influence of omitted higher-order terms in the Landau power series expansion.

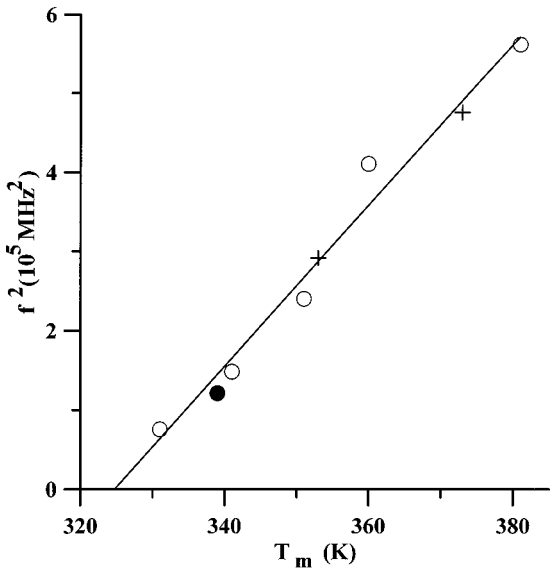

FIG. 3. Squared ultrasound frequency versus temperature of attenuation maximum obtained from temperature (open circles) and frequency (closed circle and crosses) dependences of ultrasound attenuation. Crosses correspond to crosses in Fig. 2. Straight line is a result of least-square fitting.

The above model implies the existence of a phase transition at temperature near 325 K. It is well known that there are no structural phase transitions near such temperature in the mixed crystals on the base of CeF_3 (see Ref. 25, and references therein). Our x-ray powder diffraction measurements confirm this. However, one can suggest that a superionic phase transition occurs at this temperature accompanied by changes in the character of ionic fluorine mobility.[1] In the pure CeF_3 crystal some changes in the character of the fluorine mobility were detected near 290 K in Ref. 25. To verify such suggestion we performed measurements of temperature dependences of electric conductance and nuclear magnetic resonance (NMR) in the sample under study. The ac conductance measurements were carried out using the four-probe method within a temperature range of 180–510 K. The ^{19}F NMR line shape measurements were made on a Bruker Avance400 NMR pulse spectrometer within a temperature range of 296–400 K. The results of the electric measure-

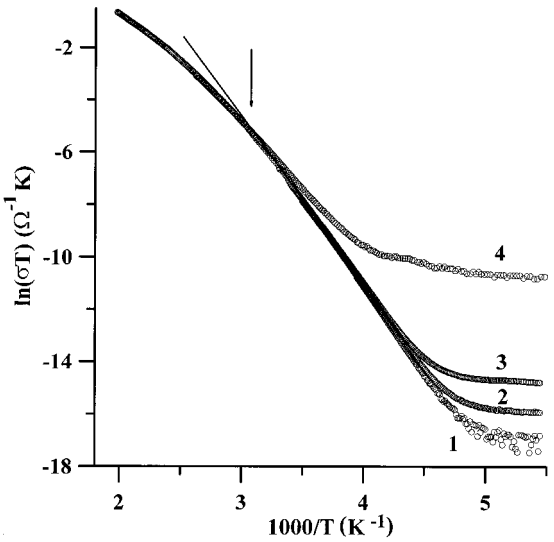

FIG. 4. Logarithm of electric conductance measured at 100 Hz (1), 1 kHz (2), 10 kHz (3), and 1 MHz (4) multiplied by temperature versus inverse temperature. Straight line shows a linear dependence. The arrow marks a temperature of the onset of curve deviation from the linear dependence.

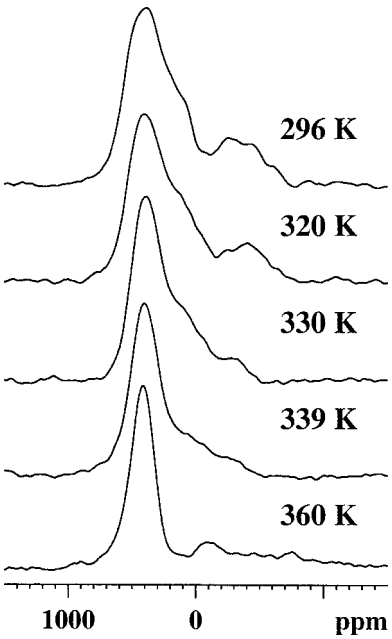

FIG. 5. ^{19}F NMR spectra at several temperatures within the range 296–360 K.

ments at four different frequencies of 0.1, 1, and 10 kHz, and 1 MHz are shown in Fig. 4. Above 230 K the sample displays high ionic conductivity that does not depend on frequency at higher temperatures in agreement with the delocalized nature of fluorine mobility. The logarithmic curves are straight lines for low frequencies between about 230 and 320 K; the enthalpy of activation calculated from these curves is equal to 0.54 eV. Note, that this enthalpy is somewhat higher than that for the corresponding temperature range in the pure CeF_3 single crystal (0.45 eV).[25] Above about 325 K the curves start deviating from the straight line revealing noticeable changes in the activation enthalpy. Drastic alterations in fluorine mobility can be also seen from the temperature dependence of NMR line shown in Fig. 5. While no remarkable changes in the NMR line shape occur between 296 and 320 K, NMR line transforms fast above 330 K manifesting alterations in the character of fluorine mobility. Thus, following other studies of trifluorides[26–28] one can assume that some change in the character of ionic mobility occurs near 330 K. Hence, the conductance measurements as well as the NMR confirm the suggestion that some superionic phase transition exists slightly above room temperature.

The frequency ω_0 defined by the relationship (6) can be treated as an analog of the soft mode for the displacive structural phase transitions.[23] However, for the structural phase transitions, the soft mode is a phonon mode with much higher frequency than compared to resonance frequencies observed here. Thus, we can speculate that low ω_0 is the attribute of superionic solids and might arise due to some collective ionic movement. It should be noted that the crystal used for the present study seems to be very suitable for observing the resonance acoustic phenomena since the background attenuation is rather weak compared to other superionic fluoride crystals (see, for instance, Ref. 18 and references therein).

In conclusion, the resonance peaks of ultrasound attenuation, which moved to higher temperatures upon increasing the sound frequency, were observed in the doped CeF_3 superionic crystal. The squared frequency versus temperature of the attenuation maximum dependence was found to be linear. The resonance ultrasound attenuation and the shift of attenuation peaks were treated within the framework of the Landau theory assuming oscillatory dynamics of the order parameter near a superionic phase transition. From the intersection of the straight line that fitted the $f^2(T_m)$ dependence with the abscissa axis, the temperature of the superionic phase transition was found to be equal to about 325 K. This agreed with the fact that no temperature driven peaks were observed on the frequency dependence of attenuation at 290 and 312 K. The saturation of the ionic conductivity, which started near 325 K, and the changes in ^{19}F NMR spectra above 330 K confirm the suggestion about a superionic phase transition. The unusually slow critical dynamics of the order parameter that gives rise to resonance ultrasound attenuation near the phase transition might be a specific feature of superionic conductors.

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[1] J. B. Boyce and B. A. Huberman, Phys. Rep. **51**, 189 (1979).
[2] D. P. Almond and A. R. West, Phys. Rev. Lett. **47**, 431 (1981).
[3] R. Bogue and R. J. Sladek, Phys. Rev. B **43**, 4408 (1991).
[4] V. V. Vorob'ev and E. V. Charnaya, Sov. Electrochem. **26**, 1214 (1990).
[5] E. V. Charnaya, Ferroelectrics **155**, 141 (1994).
[6] V. V. Vorob'ev, E. P. Lokshin, and E. V. Charnaya, Sov. Phys. Solid State **34**, 478 (1992).
[7] B. A. Huberman and R. M. Martin, Phys. Rev. B **13**, 1498 (1976).
[8] Sh. A. Asrarov, B. F. Borisov, T. Kraevskii, and E. V. Charnaya, Sov. Electrochem. **28**, 1503 (1992).
[9] G. A. Saunders, R. D. Metcalfe, M. Cutroni, M. Federico, and A. Piccolo, Phys. Rev. B **53**, 5287 (1996).
[10] N. Inoue and Y. Ogawa, Jpn. J. Appl. Phys., Part 1 **35**, 2889 (1996).
[11] M. Cutroni and A. Mandanici, Solid State Ionics **105**, 149 (1998).
[12] M. B. Salamon, in *Physics of Superionic Conductors*, edited by M. B. Salamon (Springer-Verlag, Berlin, 1979), and references therein.
[13] Y. Luspin, D. D. Meneses, P. Simon, and G. Hauret, Eur. Phys. J. B **10**, 215 (1999).
[14] M. Pavel, A. Pawlowski, Z. Zikmund, and M. Drozdowski, Solid State Ionics **91**, 161 (1996).
[15] M. Maeda, M. Takagi, and I. Suzuki, J. Phys. Soc. Jpn. **69**, 267 (2000).
[16] M. B. Salamon, Phys. Rev. B **15**, 2236 (1977).
[17] M. O. Manasreh and D. O. Pederson, Phys. Rev. B **38**, 6270 (1988).
[18] P. E. Ngoepe and J. D. Comins, Phys. Rev. Lett. **61**, 978 (1988).
[19] E. Dieulesaint and D. Royer, *Elastic Waves in Solids: Applications to Signal Processing* (Wiley, Chichester, NY, 1980).
[20] R. Truell, Ch. Elbaum, and B. B. Chick, *Ultrasonic Methods in Solid State Physics* (Academic, New York, 1969).
[21] J. Xu and R. Stroud, *Acousto-optic Devices: Principles, Design, and Applications* (Wiley, New York, 1992).
[22] A. E. Aliev, Ya. V. Burak, V. V. Vorob'ev, I. T. Lyseiko, and E. V. Charnaya, Sov. Phys. Solid State **32**, 1641 (1990).
[23] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon, Oxford, 1977).
[24] E. K. H. Salje, *Phase Transitions in Ferroelastic and Co-elastic Crystals* (Cambridge University Press, Cambridge, 1993).
[25] M. E. Omari, J. Sénégas and J.-M. Réau, Solid State Ionics **107**, 281 (1998).
[26] M. E. Omari, J. Sénégas and J.-M. Réau, Solid State Ionics **107**, 293 (1998).
[27] A. F. Privalov, H.-M. Vieth, and I. V. Murin, J. Phys.: Condens. Matter **6**, 8237 (1994).
[28] F. Wang and C. P. Grey, Chem. Mater. **9**, 1068 (1997).