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Ultrasonic Investigation of the Piezoelectric Ionic Crystal β -AgI

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Ultrasonic attenuation and phase velocity measurements as a function of temperature and frequency are reported in the β phase of AgI. Below about 50 MHz the dominant effect is the piezoelectric coupling between the mobile ions and the ultrasonic waves; an analysis similar to that of Hutson and White for piezoelectric semiconductors gives good agreement. Above 50 MHz this interaction becomes screened. An additional attenuation mechanism is observed at 540 MHz.

AgI has received considerable attention in recent years, largely because of its superionic properties. At $T_c = 420$ K, the material undergoes a first-order phase transition from the hexagonal wurtzite (β) structure¹ ($C_{6v}^4-P6_3mc$), which is the stable form at room temperature, to the body-centered-cubic (α) phase ($O_h^9-Im\bar{3}m$). This structural phase transition is accompanied by a jump in the ionic conductivity of nearly four orders of magnitude from about 3×10^{-4} to over 1 ($\Omega \text{ cm}$)⁻¹, the conductivity in the high-temperature phase being comparable to that in liquid electrolytes. However, even in the low-temperature β phase, the ionic conductivity of silver iodide is higher than in many ionic compounds.

Previous ultrasonic work² on β -AgI has been concerned with the effect on the elastic constants of the ionicity of the Ag-I bonds. The purpose of this Letter is to show that ultrasonic measurements can give information not only on lattice force constants, but also on quantities such as the dc ionic conductivity, the activation energy, and the frequency dependence of the ionic conduc-

tivity in a range not normally accessible by direct methods.

We have measured the temperature dependence of the variation in the attenuation and phase velocity of longitudinal ultrasonic waves propagating along the c axis of a number of β -AgI specimens. A standard pulse-echo transmission technique³ was used in the frequency range of 7.5 to 540 MHz. The temperature was varied between room temperature and a few degrees below T_c . Measurements could not be made above T_c since single crystals of AgI invariably crack on crossing the first-order phase boundary. The crystals were grown at the University of California (Irvine) by M. J. Delaney using a method developed by Mills.⁴ Specimens suitable for making ultrasonic measurements were formed by cleaving sections with faces perpendicular to the c axis of the as-grown crystals so that the samples were about 1 mm thick, the width being 2 to 3 mm. The results for the attenuation are shown in Fig. 1 and for the elastic constant in Fig. 2. The variation of the attenuation was measured to an accuracy of

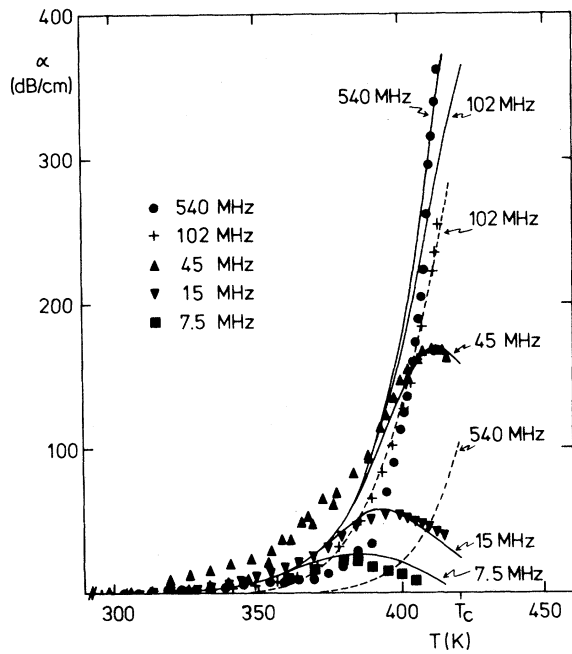


FIG. 1. The variation as a function of temperature in the attenuation of longitudinal ultrasonic waves propagating along the *c* axis in β -AgI. The points represent the experimental data, the solid curves are given by Eq. (6), and the dashed curves by Eq. (8). At 45 MHz and below, the predictions of Eq. (6) and (8) are virtually identical and therefore only one set of theoretical curves is shown.

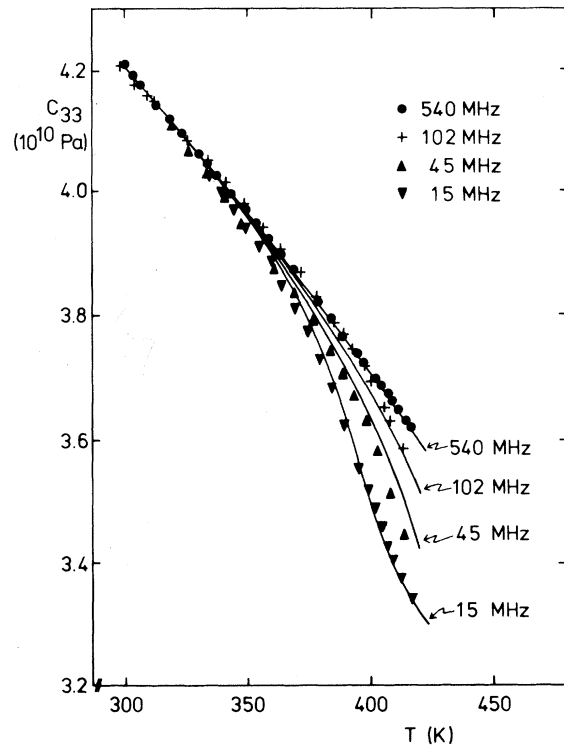


FIG. 2. The temperature dependence of c_{33} in β -AgI. The points represent the experimental data and the solid curves are given by Eq. (7).

1 dB. The scale of the ordinate in Fig. 2 was determined by an absolute measurement of the velocity at 300 K and 540 MHz.

Two points are to be emphasized in Fig. 1. First, there is a maximum in the low-frequency data. It will be shown that this occurs when the frequency of the wave is equal to the dielectric relaxation frequency which is the ratio of the conductivity σ to the dielectric constant $\epsilon\epsilon_0$. The second point is that there is a temperature range where the high-frequency attenuation is lower than it is at low frequencies. This suggests that there is a breakdown in the coupling at high frequencies. Before considering these features in more detail, the basic coupling mechanism which gives rise to the variation in the attenuation and the elastic constant must be discussed.

In a medium which is piezoelectric, a propagating acoustic wave may create an internal electric field so that, if the medium is also conducting, the acoustic wave is coupled to the movement of charged carriers, modifying the attenuation and phase velocity. The theory of this effect has been

developed by Hutson and White⁵ for the case of ultrasonic propagation in piezoelectric semiconductors. Since β -AgI belongs to a piezoelectric class of materials and has an appreciable conductivity, albeit ionic, it is reasonable to consider a similar calculation in the interpretation of our results.

In the temperature range of the present experiments, it is known that the ionic conductivity in AgI occurs via Frenkel defects.^{6,7} Furthermore, the mobility of vacancies has been shown to predominate over that of interstitial ions.⁷ A simple hopping model for the dc conductivity gives the formula⁸

$$\sigma_v = (A/k_B T) \exp[-(\frac{1}{2}E_F + E_v)/k_B T], \quad (1)$$

where E_F is the energy required to create a Frenkel defect, E_v is the hopping activation energy for vacancies, and $A = N_0(ea)^2\nu_0$. N_0 is the concentration of Ag sites, e is the ionic charge, a is the hopping distance, and ν_0 is the attempt frequency.

The total current density in the sample can be

written as the sum of two contributions:

$$J = \sigma_v E - e \mathcal{D}_v \partial n_v / \partial z. \quad (2)$$

The first term is due to the hopping of vacancies and the second term accounts for vacancy diffusion which occurs because of the concentration gradient $\partial n_v / \partial z$. \mathcal{D}_v is the diffusion constant which is the diffusion constant which is described by the relation $\mathcal{D}_v = \mathcal{D}_{0v} \exp(-E_v/k_B T)$, where $\mathcal{D}_{0v} = a^2 \nu_0$.

The coupling between the elastic and electrical properties originates in the usual equations of state of a piezoelectric medium⁹:

$$T = cS - \eta E, \quad (3)$$

$$D = \eta S + \epsilon \epsilon_0 E. \quad (4)$$

Here T , S , c , and η are the appropriate elements of the stress, strain, elastic constant, and piezoelectric tensors, respectively, and D and E are the electric displacement and field. With use of Eqs. (2), (3), and (4), the equation of continuity, and Gauss's theorem, an expression can be obtained for the complex elastic constant

$$c^* = c \left[1 + \frac{\eta^2}{\epsilon \epsilon_0 c} \left(1 - \frac{1}{i\omega\tau_c(1-i\omega\tau_D)} \right)^{-1} \right], \quad (5)$$

where c^* has been expressed in terms of two characteristic relaxation times for conductivity ($\tau_c = \epsilon \epsilon_0 / \sigma_v$) and diffusion ($\tau_D = \mathcal{D} / v_s^2$). Here v_s is the velocity of sound. These two relaxation times can be calculated from the experimental data summarized in Table I with use of the above expressions for σ_v and \mathcal{D}_v . The values of τ_c and τ_D are given for two temperatures in Table II, which shows that the ultrasonic frequency ω can be comparable to $1/\tau_c$ but that $\omega\tau_D$ is always much less than unity. Thus the diffusion term appears to be negligible in (5), which then yields for the ultrasonic attenuation and elastic constant:

$$\alpha = \frac{\kappa^2}{v_s} \frac{\omega^2 \tau_c}{1 + \omega^2 \tau_c^2}, \quad (6)$$

$$c = c_A \left\{ 1 + \kappa^2 \frac{\omega^2 \tau_c^2}{1 + \omega^2 \tau_c^2} \right\}. \quad (7)$$

TABLE I. Experimental data for β -AgI.

E_F (eV)	E_v (eV)	A/k_B ($\Omega^{-1} \text{ m}^{-1} \text{ K}$)	ϵ	v_s (m s^{-1})
0.6 ^a	0.5 ^a	3.7×10^{10} ^a	7 ^a	2.71×10^3 ^b

^aRef. 7.

^bThis work.

Here $\kappa^2 = \eta^2 / \epsilon \epsilon_0 c_A$, α is the power attenuation coefficient, and c_A includes the usual anharmonic contribution to the elastic constant.

With use of κ as an adjustable scaling parameter and taking the values of all other required parameters from the experimental data of Table I, the set of solid curves shown in Fig. 1 were obtained. The figure shows that there is good agreement between theory and experiment for the lowest frequencies. Note that the position of the maximum in the attenuation is given exactly by the theory using only the published values of the conductivity and the dielectric constant. From the maximum value of the attenuation at 45 MHz, the coupling constant κ^2 is found to be 0.088. Our value of κ is about twice the value quoted by Fjeldly and Hanson.²

The curves in Fig. 2 which describe the variation of the elastic constant c_{33} are obtained from Eq. (7), where c_A is given by the usual linear high-temperature behavior,¹⁰ $c_A = c_0 - \gamma T$. By fitting these equations to the data, it was found that $c_0 = 5.20 \times 10^{10}$ Pa and $\gamma = 0.45 \times 10^8$ Pa K^{-1} . It should be noted that the values of the parameters κ^2 and τ_c were previously determined from the attenuation results and the data in Table I; thus they were not adjusted in obtaining the fit shown in Fig. 2. The agreement can be seen to be good.

There remains a feature of the attenuation data which is not explained by the theory presented thus far. For the data at the two highest frequencies there is a range of temperature in which the measured attenuation decreases as a function of frequency, in contrast to the solid theoretical curves in Fig. 1. This implies that there is a screening effect. Our results can be explained if the ionic conductivity is taken to have a frequency dependence of the form $\sigma(\omega) = \sigma(0) / (1 - i\omega\tau)$ with a temperature-dependent relaxation time $\tau = \tau_0 \exp(E_A/k_B T)$. In this case, the full expression (5) applies if the substitution $\tau = \tau_D$ is made.⁵

TABLE II. Values of the relaxation times for conductivity (τ_c) and diffusion (τ_D) calculated from the data in Table I.

T (K)	τ_c (s)	τ_D (s)
300	1.4×10^{-5}	7.3×10^{-19}
420	2.8×10^{-9}	1.8×10^{-16}

The attenuation then obeys the relation

$$\alpha = \frac{\kappa^2}{v_s} \frac{\omega^2 \tau_c}{\omega^2 \tau_c^2 + (1 + \omega^2 \tau_c \tau)^2} \quad (8)$$

With use of Eq. (8), the dashed curves shown in Fig. 1 were obtained.¹¹ A good fit was found for the 102-MHz curve, giving $\tau_0 = (1.0 \pm 0.3) \times 10^{-12}$ s and $E_A = 0.3 \pm 0.03$ eV. It is interesting that τ_0^{-1} (34 cm^{-1}) corresponds to a frequency in the infrared range. Although it might be expected that the relaxation time τ is equal to the hopping time, there appears to be little theoretical justification for this¹²; models which relate the frequency dependence of the conductivity to a hopping mechanism give different dependence on ω .¹³ However, a Drude-like form for $\sigma(\omega)$ is found by considering theories involving a lifetime of the ion in a free-ion-like state.¹⁴ By analogy, we suggest that the hopping of vacancies is limited by a characteristic lifetime which describes the time between the creation of the vacancy and its recombination with an interstitial ion. Thus the relaxation time τ may be related to the vacancy lifetime. Since this lifetime depends inversely on the number of interstitial ions available for recombination [which in our case is the number of Frenkel defects, $N_0 \exp(-E_F/2k_B T)$], τ would then be expected to be proportional to $\exp(E_F/2k_B T)$. E_A determined by the 102-MHz data is in excellent agreement with half the value of E_F (Table I) as predicted by this hypothesis. It should be noted that Drude-like behavior has already been observed in the conductivity of α -AgI (Ref. 15) and RbAg_4I_5 (Ref. 16) at about 10 GHz and 20 MHz, respectively. However, because of some basic differences in the conduction mechanism in these two superionic conductors (e.g., the number of mobile ions is much larger than in β -AgI), a simple relationship between the different relaxation times is not expected.

At 540 MHz, the dashed curve in Fig. 1 falls well below the experimental points, indicating that another attenuation mechanism is involved at high frequencies. The most plausible explanation is that this additional contribution is due to critical attenuation near the crystallographic transition¹⁷; experiments at higher frequencies are currently in progress to clarify this point.

In summary we have shown that the variation of the velocity and the attenuation of ultrasonic waves propagating along the c axis of β -AgI crystals is well explained by the piezoelectric coupling to the movement of Ag^+ ions, at least for frequencies up to about 200 MHz. This is the first

time that piezoelectric coupling between ultrasonic waves and ionic carriers has been invoked to explain the ultrasonic properties of ionic conductors. Above 50 MHz, there is a range of temperature over which the measured high-frequency attenuation is less than at low frequencies, implying a screening effect; this may be explained if the ionic conductivity is taken to have a frequency dependence of the Drude type. On the basis of this interpretation, an additional coupling mechanism must be involved at high frequencies (> 200 MHz).

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¹²The only case in point appears to be a calculation by I. Z. Kostadinov [*Phys. Lett.* **64A**, 85 (1977)], who found a frequency-dependent conductivity of the Drude type on the basis of a hopping model in which the hopping proceeds via two wells of different depths U and V . His "relaxation time" is equal to a hopping time which is proportional to $\exp[(U+V)/2k_B T]$. It is interesting to note that our value of E_A is consistent with his results if $V = 0.1$ eV, U being given by the accepted value for vacancy diffusion (0.5 eV).

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Macroscopic Electron Lattice on the Surface of Liquid Helium

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A nonlinear theory of the capillary waves accounts for the macroscopic lattice formation on the electron-charged surface of liquid helium observed in a recent experiment. The lattice allows both shear and compressional lattice waves to propagate.

There has been a great deal of interest in systems consisting of a layer of electrons on the surface of liquid helium. Recently, Wanner and Leiderer¹ found experimentally that a macroscopic dimple lattice was created at an electron-charged interface between ³He and ⁴He. The theory presented here accounts for most of the observed results. A preliminary discussion of the present problem was given by Gor'kov and Chernikova.²

Consider the liquid helium filling a volume $-z_0 \leq z \leq 0$. The surface of the liquid is in the x - y plane ($z=0$) when it is not disturbed. The surface of the liquid is charged with electrons. The electric field (E_+ at $z>0$, and E_- at $z<0$) is applied in the vertical, z , direction to bind the electrons to the surface.

The nonlinear dispersion relation of the capillary waves of frequency ω , as a function of the

wave vector \vec{k} , is given by^{3,4}

$$\omega^2(\vec{k}) = g|\vec{k}| - (1/4\pi\rho)(E_+^2 + E_-^2)|\vec{k}|^2 + (\tau/\rho)|\vec{k}|^3, \quad (1)$$

where ρ is the density of the liquid, g the gravity constant, and τ the surface tension. The Rayleigh-Taylor instability grows, i.e., $\omega^2 < 0$ near $|\vec{k}| = k_0$, when $\frac{1}{2}(E_+^2 + E_-^2) > 4\pi g\rho/k_0$, where $k_0^2 = \rho g/\tau$. The nonlinear behavior of this instability will be analyzed here.

It is assumed that the liquid is incompressible and that the electrons redistribute instantaneously in such a way that the electrostatic potential is always constant along the surface. The large electron mobility ensures that latter assumption. By employing the basic equations and the procedure described by Mima and Ikezi,⁵ the equation governing the surface deviation, $z = a(x, y, t)$, is found to be

$$\begin{aligned} a_{tt} = & -g\frac{P}{T}a + \frac{E_+^2 + E_-^2}{4\pi\rho}P^2a + \frac{(E_+^2 - E_-^2)}{8\pi\rho}\frac{P}{T}[2PTaPTa - 2aP^2a + (PTa)^2 + a_x^2 + a_y^2] \\ & + \frac{E_+^2 + E_-^2}{4\pi\rho}\frac{P}{T}[PT(-\frac{1}{2}a^2P^2a + aPTaPTa - aP^2aPTa) + \frac{1}{2}a^2P^3Ta + (a_x^2 + a_y^2)PTa \\ & \quad + (PTa)(PTaPTa - aP^2a)] \\ & + \frac{\tau}{\rho}\frac{P}{T}[a_{xx}(1 - \frac{3}{2}a_x^2 - \frac{1}{2}a_y^2) + a_{yy}(1 - \frac{3}{2}a_y^2 - \frac{1}{2}a_x^2) - 2a_{xy}a_xa_y]. \end{aligned} \quad (2)$$

Here, P and T are operators defined by

$$P^2 = -\nabla_{\perp}^2 = -(\partial^2/\partial x^2 + \partial^2/\partial y^2),$$

and $T = \coth(z_0P)$, the suffixes x , y , and t indicate partial derivatives with respect to those variables, and the P and T enclosed in () do not operate outside of the heavy parentheses. The linear

terms of this equation give us the dispersion relation (1). The nonlinear terms which are important for discussing the Rayleigh-Taylor instability are retained.

Because the parameter range of interest is $\frac{1}{2}(E_+^2 + E_-^2) \sim 4\pi g\rho/k_0$ and $|\vec{k}| \sim k_0$, the waves of the