

Order and disorder in high-temperature long-wave acoustics (I): dielectrics, semiconductors, and conductors

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The linear long-wave approximation is used to analyze the classical interaction between elastic waves and local disorder in dielectric, semiconducting, and metallic crystals. It is shown that carriers of thermal and nonthermal disorder provide significantly different contributions to the acoustic parameters of crystals such as the velocity of sound and the sound attenuation coefficient. The effect of direct and indirect interactions between elastic waves and the ensemble of carriers of disorder on the attenuation of sound is examined. In the former case, deformation by the wave modifies the motion of the carriers of disorder themselves, whereas in the latter case the elastic wave interacts with quasiparticles in the crystal, and the presence of disorder is seen as a change in the character of motion of these quasiparticles. The effects of high concentrations of carriers of disorder produced by melting one of the sublattices of superionic crystals are also described.

1. GENERAL INTRODUCTION

According to the dictionary,¹ the word 'order' has a number of meanings. First, it means a set of objects arranged in sequence one after another and 'not higgledy-piggledy.' Second, it means a picture of disposition or method of arrangement, and so on. Third, it means 'a sequence of actions in accordance with a predetermined rule.' This diversity of meaning of the word 'order' is reflected in the terminology of physics.

However, these definitions do not provide us with a key to the *measurement* of order. A measure of order can be the degree of deviation from order, i.e., the magnitude of disorder. The third definition of order, which is based on the possibility of using specific algorithms, is the most suitable from the standpoint of physical disorder. A reduction in order can then be treated as a signal that we have to introduce probabilistic concepts. The simplest example is provided by the position coordinate that represents the localization of an impurity atom. This is determined by the potential distribution in the unit cell and by the properties of the impurity. Disorder is then seen as the uncertainty in the cell number. Depending on its source, disorder can be subdivided into 'natural' and 'artificial.' The former includes disorder due to thermal motion. For example, the carriers of disorder in crystals include thermal point defects such as crowdions, interstitial atoms, vacancies, and so on. So long as the number of such carriers of point disorder is small in comparison with the total number of atoms, they may be looked upon as an 'impurity' of disorder in order, and this provides us with a mathematical basis for a description of their manifestations. Experiment shows that the thermal disorder 'impurity' is small throughout the temperature range in which crystals exist, so that the concepts of short- and long-range order in the crystal sense can still be used, and the crystal structure can be treated as the zero-order approximation (a possible exception is the temperature interval adjacent to the melting point T_m). Artificial disorder produced, for example, by introducing impurities into a crystal, can be described in a similar way. Acoustic measurements enable us, at least in principle, to separate these contributions and to estimate order quantita-

tively by establishing the necessary experimental conditions.

Processes involving estimates and applications of order and disorder can also be described by adopting the reverse approach whereby perfect disorder is taken as the zero-order approximation. For example, if we transfer our attention from a gas to a liquid, we find that definite ordering immediately takes place because of the sharp reduction in the free volume as compared with a gas, and symptoms of short-range order appear in the structure, e.g., the atoms are no longer uniformly distributed in space, there is a preferred number of neighbors (coordination number), and so on. This type of geometric ordering is fundamental in densely-packed metallic alloys and is very significant in melts of semimetals and semiconductors, which will be discussed in some detail below.

There have been frequent attempts (see, for example, the review in Ref. 2) to provide a general theoretical description of the relationship between order and disorder that would be suitable for media with long- and short-range order, but clear recipes are still lacking.

Experimental methods of studying disorder in order and of manifestations of order (in the senses introduced above) in disorder are usually subdivided into direct and indirect. Direct methods are based on studies of x-ray and neutron scattering by given spatial structures, whereas indirect methods rely on studies of the so called structure-sensitive macroscopic properties, combined with searches for correlations between singularities in the dependence of these properties on external factors and structure.

There is a thin dividing line between direct and indirect methods from the standpoint of the amount of information that can be extracted about order and disorder in disordered media. We know that the measured scattered intensity as a function of the angle θ and energy E can be transformed into the static $S(\mathbf{k})$ and dynamic $S(\mathbf{k}, E)$ structure factors that are related to the static and dynamic pair correlation functions $g(r)$ and $G(r, t)$ by the expressions (see for example, Ref. 3):

$$S(\mathbf{k}) = 1 + \rho \int (g(r) - 1) \exp(i\mathbf{k}\mathbf{r}) d\mathbf{r}, \quad (1)$$

$$S(\mathbf{k}, \omega) = \frac{1}{2\pi} \int (G(r, t) - \rho) \exp(i\mathbf{k}\mathbf{r} - i\omega t) d\mathbf{r} dt, \quad (2)$$

where \mathbf{r} is the position vector, ρ is the density, ω is the angular frequency, $k = 4\pi \sin(\theta/2)/\lambda$, and λ is the wavelength. The expressions given by (1) and (2) provide us with the justification for referring to methods based on scattering as direct methods of studying structure. However, the derivation of these two expressions relies on a number of assumptions that are not satisfied in experiments.³ These assumptions are: no multiple scattering, no absorption of energy, no containers or windows, and so on. As noted in Ref. 3, this is as good as saying that there is no sample! Additional problems arise when $S(\mathbf{k})$ and $S(\mathbf{k}, \omega)$ are estimated for \mathbf{k} tending to 0 (but is not actually equal to 0) in which case this range of \mathbf{k} reflects the specificity of short-range order. The limiting value $S(0)$ can be obtained from indirect measurements, using the thermodynamic relation

$$S(0) = k_B T \rho N_A / MK, \quad (3)$$

where k_B is the Boltzmann constant, K is the bulk modulus, T is the temperature, N_A is the Avogadro number, M is the atomic weight, and the intermediate $S(\mathbf{k})$ are subject to considerable uncertainty.

The use of the methods of molecular dynamics to augment diffraction experiments has led to a significant improvement in the overall situation, but unambiguous conclusions have not been possible for disordered close-packed media. This question is examined in detail in Ref. 3 in the case of liquid sulfur for which diffraction data suggest a structure consisting of S_8 rings and, possibly, S_6 as well.

Similar problems arise in the interpretation of diffraction experiments for practically all media in which melting is accompanied by a change in structure. These media include semimetals (Bi, Sb) and semiconductors (Ge, Si, etc.), since the diffraction peaks of these melts have fine structures that are difficult to interpret unambiguously. For example, the hypothesis of cluster structure of such melts, i.e., the suggestion that the melts contain regions that float in the closely-packed matrix⁴ and retain condensed-phase order, has again found wide acceptance. This approach has been adopted by Regel⁵ and Glazov^{5,6} as a means of explaining the temperature behavior of electrical conductivity and viscosity of liquid semiconductors near the melting point. The same approach was used in Ref. 7 to explain the temperature dependence of the velocity of sound in molten semimetals and semiconductors. Mishin and Razumovskii⁸ have suggested that the cluster model could be extended to all alloys, and have used this as a basis for a new theory of melting and premelting, although the model itself is experimentally invalid when it is extended to all melts. Additional arguments in support of clusters can be found in Ref. 9.

There is, however, a whole range of results that do not fit the cluster model of order in disorder. For example, x-ray diffraction was used in Ref. 10 to investigate liquid tin in the temperature range 300–1700 °C. It was found that a change in temperature had practically no effect on the position of the first diffraction peak, i.e., the most probable separation between neighboring atoms and the root mean square separation remained unaltered to within experimental error. Although the second peak on the radial distribution function is broader than the first, it was suggested that the second preferred separation between atoms was also unaltered.

Direct measurements of the relative change in macroscopic volume between 300 and 1700 °C yield a figure of

14.6%. This corresponds to a 4.7% change in interatomic separation, which is much greater than the result deduced from diffraction experiments.

Similar data have also been obtained for tellurium which metallizes on melting. For temperatures in the range 773–1073 K, the position of the first and second peaks on $g(r)$ did not change to within ± 0.02 Å although measurements of density as a function of temperature suggest that there is a small increase in density near the melting point and that the density decreases almost linearly after passing through a flat maximum.¹¹ If we proceed in the spirit of cluster models, we find that thermal motion is of the solid-state (vibrational) type (in the clusters themselves) and of the translational (diffusion) type between clusters which are structures containing up to a hundred atoms organized according to the type of the corresponding crystal. This means that an intensification of thermal motion in a cluster should be accompanied, depending on the type of solid, by an increase in atomic separation. Moreover, Turner's calculations¹² show that the appearance of crystal 'fragments' in disordered structures as indicators of the onset of order leads to anomalously high structure factors due to correlations between concentration and fluctuations in concentration, whereas it is noted in Ref. 2 that this approach leads to the problem of 'special' atoms on the surface of clusters, whose properties have to be taken into account. Model descriptions are also impossible to avoid in attempts to deduce information about the thermal motion of atoms from direct measurements obtained by studying the behavior of the pair autocorrelation function which can be deduced from the dynamic correlation function $G(\mathbf{r}, t)$ (Ref. 12).

These problems are discussed in Ref. 13 where it is noted that the long-term asymptotic form of the velocity autocorrelation function is $t^{-3/2}$ (which is typical for diffusion spreading of correlations) has been experimentally confirmed, but only for liquid sodium (t is the time of observation). In other experiments, it has been difficult to achieve an unambiguous interpolation of $S(\mathbf{k}, \omega)$ between $\mathbf{k} = 0$ and \mathbf{k} that would fit experimental data, and to verify the asymptotic form $t^{-3/2}$. For intermediate values of t , it is even more difficult to draw from diffraction data any conclusions about the nature of thermal motion in structurally disordered media. Diffraction experiments only confirm that, in high-temperature disordered media (melts of elementary materials), and for short periods of observation of a particle, the particle executes vibrational motion, whereas diffusion-type motion occurs for $t \rightarrow \infty$. It has not been possible to deduce from experimental data the form of either type of motion, or of transitions between them, and a large number of models has been put forward (see the reviews in Refs. 5 and 6).

For example, Bar'yakhtar *et al.*¹⁰ have interpreted their experimental data (showing that the mean atomic separations are temperature independent) in terms of the Frenkel hole model of a liquid¹⁴ although it is well known that there is a whole range of experimental factors that do not fit this model.^{5,6}

Of course, model descriptions are also used in indirect methods of measuring order and disorder parameters. However, the relative simplicity and high precision of experiments have produced reliable evidence for the dependence of order parameters on external conditions and for the effect of this on a range of macroscopic properties. Comparison be-

tween direct and indirect measurements can be used to draw more reliable conclusions about changes in the structure of media under investigation. Moreover, since indirect measurements yield numerical values of macroscopic variables, rigorous thermodynamic relations can be used to verify model descriptions of order and disorder. Results obtained by indirect acoustic methods of studying equilibrium and nonequilibrium of partially and completely disordered media will be described below. We shall use the elastic moduli c_{ij} and the bulk modulus K , on the one hand, and the sound attenuation coefficient α , on the other, as functions of external factors such as temperature, vibration frequency, pressure, and so on.

In principle, the relationship between order and the volume compressibility can be obtained from statistical thermodynamics. The result is¹⁵

$$K^{-1} = \frac{M}{k_B T \rho N_A} \left[1 + \int_0^\infty (g(r) - 1) r^2 dr \right]. \quad (4)$$

This relation is rigorous, but not very useful in specific calculations because, to establish short-range order effects in compressibility, we must have a very precise knowledge of $g(r)$, which is not provided by diffraction experiments.

A considerable amount of information can therefore be extracted by comparing experimentally determined functions $c_{ij}(T)$ and $K(T)$ with theoretical calculations based on different models of disorder, and also by comparing the behavior of these quantities with data obtained from other structure-sensitive properties. This approach enables us to determine relatively small changes in order-disorder relations, especially for topologically disordered media. In crystals, on the other hand, such measurements are found to be less informative because the contribution of growing thermal disorder is masked by increasing anharmonicity of vibrations.

Moreover, if we compare changes in elastic moduli observed during the transition from crystal to melt, and from amorphous body to melt, in materials in which there is no change in the type of interaction, we can isolate contributions due to the loss of long-range order in the first case, and the onset of intensive translational motion in the second.

As far as the kinetics of different processes in disordered media is concerned, this is particularly clear in the sound attenuation coefficient α . The problem usually consists of choosing the optimum experimental conditions to ensure that the contributions of particular processes can be isolated, and of calculating α for different models of disorder.

In the long-wave limit, the acoustic description can be applied not to the individual local manifestations of disorder, but to the disorder parameters averaged over the volume containing either a large number of structural units of disorder (when these can be readily identified) or simply a large number of atoms.

Another important limitation of the range of questions examined in this review and, subsequently, in Ref. 15a, involves the temperature ranges. The high-temperature approximation will be used whenever we can ignore quantum effects inherent in disordered systems, especially different modifications of two-level models that are so effective in relation to low-temperature anomalies.

By restricting the temperature range at the high end we ensure that the condensed state of matter is preserved (and there are no critical phenomena).

We have already noted that the use of crystal order as the zero-order approximation to disorder in crystals produces a sufficiently consistent theoretical description of these processes.

In the case of the liquid state (topological disorder; cf. Ref. 15a), we shall concentrate our attention on experimental results obtained by varying different factors, and the comparison of theoretical ideas with experimental data will be largely qualitative in view of the foregoing remarks.

Because of the great diversity of possible situations, an effective approach is to use the thermodynamic description in the spirit of relaxation models developed for liquids and gases by Mandel'shtam, Leontovich, and Knezer, and subsequently extended by many others (see, for example, Ref. 16). If we describe nonequilibrium states by the Gibbs local equilibrium distribution,¹⁷ and if we use the hydrodynamic approximation, we can also take transport processes into account together with the additional (as compared with the usual thermodynamic variables such as temperature T and strain u_{ik}) variable ξ that characterizes the internal state of the system, i.e., the specific physical model of disorder. The basic assumption for this type of analysis is that the system consists of several subsystems in which the approach to equilibrium occurs in two stages: partial equilibrium is initially established in the subsystems, and is subsequently followed by complete statistical equilibrium.

The procedure describing the relaxation process includes a perturbation-type series expansion of a thermodynamic potential, e.g., the free energy F per unit volume \bar{V} , the local entropy balance equation, the relaxation equation, and the condition for local equilibrium.

Let us now write down the expansion for the free energy in powers of perturbations produced by an elastic wave, taking into account the internal parameter in a form convenient for both solids and liquids.¹⁸ In the isotropic case we have

$$\begin{aligned} F = F_0 + \frac{K}{2} u_{ll}^2 + G(u_{ik} - \frac{1}{3} \delta_{ik} u_{ll})^2 \\ - K \beta_T u_{ll} \delta T + \frac{1}{2} \left(\frac{\partial^2 F}{\partial T^2} \right)_0 \delta T^2 + \left(\frac{\partial^2 F}{\partial \xi_r \partial T} \right)_0 \delta T \delta \xi_r \\ + \left(\frac{\partial^2 F}{\partial u_{ik} \partial \xi_r} \right)_0 u_{ik} \delta \xi_r + \frac{1}{2} \left(\frac{\partial^2 F}{\partial \xi_r^2} \right)_0 \delta \xi_r^2 + \dots \end{aligned} \quad (5)$$

whereas in the anisotropic case we must replace the second and third terms with

$$\frac{1}{2} \lambda_{ik, mn} u_{ik} u_{mn} - \lambda_{ik, mn} \beta_{mn} \delta T u_{ik},$$

where the subscript 0 indicates that the corresponding value is taken in the state unperturbed by the elastic wave, G is the shear modulus, δ_{ik} is the Kröner symbol, β_T is the volume expansion coefficient, and ξ_r is the internal parameter of the r th subsystem.

All the expansion terms, with the exception of those containing the internal parameters, correspond to the free-energy expansion given in Ref. 19.

The local entropy-balance equation is¹⁷

$$\frac{\partial S_p}{\partial t} - \frac{\partial j_{S_i}}{\partial x_i} = \sigma_{out}^S + \sigma_{in}^S, \quad (6)$$

where S_p is the entropy density, j_S is the entropy flux density, σ_{out}^S and σ_{in}^S are the densities of external and internal entropy sources, and x_i are the cartesian coordinates.

As far as the time rate of change of the internal parameter ξ_r is concerned, it is assumed that the rate at which an internal parameter tends to equilibrium is

$$\frac{d}{dt}\xi_r = -\frac{1}{\tau_r}(\delta\xi_r - \delta\xi_r^e), \quad (7)$$

where $\delta\xi_r$ is the instantaneous deviation off the internal parameter ξ_r from its value ξ_r^0 in the absence of perturbation and ξ_r^e is the new equilibrium value in the presence of the wave. If the perturbation is a plane harmonic wave of frequency ω , and if we neglect transport processes, we find that the sound attenuation coefficient α and the change Δs in the velocity of sound due to relaxation processes¹⁸ are respectively given by

$$\alpha_r = \frac{L_r}{2\bar{V}\rho s^3 C_{\bar{V}}^* C_{\bar{V}}^*} \frac{\omega^2 \tau_r}{(\partial^2 F / \partial \xi_r^2)_0} \frac{1}{1 + \omega^2 \tau_r^2}, \quad (8)$$

$$\Delta s = \frac{L_r}{2V\rho s C_{\bar{V}}^* C_{\bar{V}}^*} \frac{1}{(\partial^2 F / \partial \xi_r^2)_0} \frac{1}{1 + \omega^2 \tau_r^2},$$

where

$$L_r \equiv \left[K\beta_r T \left(\frac{\partial^2 F}{\partial \xi_r \partial T} \right)_0 \delta_{ik} - C_{\bar{V}}^* \left(\frac{\partial^2 F}{\partial \xi_r \partial u_{ik}} \right)_0 \right]^2,$$

$$C_{\bar{V}}^* = C_{\bar{V}} + T \left(\frac{\partial^2 F}{\partial \xi_r \partial T} \right)_0^2 \left[\left(\frac{\partial^2 F}{\partial \xi_r^2} \right)_0 \right]^{-1}, \quad \tau_r = \tau_r' \frac{C_{\bar{V}}^*}{C_{\bar{V}}}, \quad (9)$$

$$\alpha = \sum_r \alpha_r,$$

in which $C_{\bar{V}}$ is the specific heat at constant volume \bar{V} and s is the velocity of sound for longitudinal ($i = k$) or shear ($i \neq k$) waves. In the anisotropic case, we must replace $K\beta_r$ with $\lambda_{ik,mn} \beta_{mn}$ in the brackets in the first term.

2. ACOUSTIC EFFECTS IN MEDIA WITH LOCAL DEPARTURE FROM CRYSTALLINE ORDER

Any type of defect, namely, point, line (dislocations), or volume, i.e., clusters of defects (fluctuations in concentration) can act as a localized 'impurity' of disorder in crystalline order. A progressive elastic wave interacts with defects, becomes attenuated as a result, and its propagation velocity changes. These changes in the elastic-wave parameters provide us with a way of investigating the manifestations of disorder in crystals by acoustic methods. The whole range of local manifestations of disorder in acoustic properties can be divided into two major groups, namely, direct and mediated interactions between elastic waves and defects.

The first group includes interactions that produce a change in the individual characteristics of defects. Thus, de-

formations produced by an elastic wave result in the displacement of impurity atoms within the unit cell or in the vibrational motion of dislocations; deformations and changes in temperature in the wave field modulate the probability of creation and annihilation of thermal-fluctuation point defects; and so on.

Mediated mechanisms are those in which an elastic wave interacts not with the local manifestations of disorder themselves, but with collective excitations, phonons, electrons, and so on, which are present even in the perfect (in the sense of order) crystal. The role of disorder then reduces to a change in the parameters of this interaction.

The study of these mechanisms of disorder in perfect crystals is a substantial part of the physics of real crystals. Some of them have often been discussed in reviews and monographs.²⁰⁻²⁴ We shall therefore ignore many important factors, such as, for example, the dislocation and domain mechanisms, and will confine our attention to estimates of these contributions in the high-temperature range in the context of particular experiments.

In the following sections we will discuss the most universal mechanisms of local disorder that operate in a wide range of temperatures and remain significant at high temperatures. Our aim will be to explore their usefulness in quantitative estimates of local disorder.

2.1. Manifestations of local disorder in crystalline dielectrics

2.1.1. The most universal mechanism of interaction of elastic waves with perfect crystals generally and dielectric crystals in particular is the interaction with the thermal vibrations of the crystal atoms. When the wavelength of an elastic wave is much greater than the wavelength of collective vibrations, the wave may be looked upon as a classical field that produces a deviation of the phonon distribution function from its equilibrium form. The new distribution function is established by phonon collisions, but this does not occur in phase with the strain produced by the wave. The result is the absorption of the elastic-wave energy, first considered by Akhiezer in Ref. 25.

In the other limiting case, the elastic wave may be looked upon not as a classical field, but as a beam of artificial phonons, and the absorption of sound is determined by three-phonon processes controlled by special selection rules (this is the Landau-Rumer mechanism²⁶).

In the long-wave limit, the presence of local disorder in the form of impurity atoms without internal degrees of freedom ensures that, in addition to phonon-phonon collisions with frequency $\Gamma_{ph,ph}$, the establishment of the new phonon equilibrium function is affected by phonon-impurity collisions of frequency $\Gamma_{ph,i}$ (Refs. 27 and 28).

This mechanism for the effect of local disorder on the acoustic properties of crystals is a typical example of a mediated contribution of disorder, since the direct interaction between elastic waves and point defects does not occur in the system. We also note that the onset of local disorder, especially for high concentrations c of disorder, also leads to a change in the average properties of the crystal (its density and elastic moduli), but these changes usually have practically no effect on the interaction between elastic waves and thermal lattice vibrations, and can be described by the effec-

time-medium model.²⁹ We also note that the quasilocal oscillations associated with point defects are relatively unimportant for these processes because, in real experimental situations, the masses and force constants of the defects and of the unit cell of the original lattice are not very different, which means that the local oscillation frequencies are not very different from the Debye frequencies.³⁰

The effect of local disorder on the Akhiezer attenuation of sound is particularly well defined for pure shear waves, since the elastic strain $u_{ik}(\mathbf{r}, t)$ then affects only the phonon frequency $f_{\text{ph}}(\mathbf{k}_{\text{ph}}, \mathbf{r}, t)$ relative to the unperturbed frequency $f_{\text{ph}}^0(\mathbf{k})$ (Ref. 25):

$$f_{\text{ph}}(\mathbf{k}_{\text{ph}}, \mathbf{r}, t) = f_{\text{ph}}^0(k_{\text{ph}})(1 + \Lambda_{ik}^{\text{ph}} u_{ik}(\mathbf{r}, t)), \quad (10)$$

and the new distribution function is established as a result of normal processes in the phonon subsystem and the Rayleigh scattering of phonons by impurities,^{27,28} where Λ_{ik}^{ph} is the phonon deformation potential and k_{ph} is the phonon wave vector (indices characterizing the phonon branch are omitted).

If $\Gamma_{\text{ph},i} \gg \Gamma_{\text{ph,ph}}$, then the characteristic time constant for the establishment of the equilibrium phonon distribution function is controlled exclusively by $\Gamma_{\text{ph},i}$ (Ref. 28)

$$\Gamma_{\text{ph},i}(k_{\text{ph}}) = \left(\frac{\Delta m_{\text{cell}}}{m_{\text{cell}}} \right)^2 c(1-c) s a^3 k_{\text{ph}}^4 \quad (11)$$

where m_{cell} is the mass of a unit cell, Δm_{cell} is the change in the mass of the cell due to the introduction of the point defect, and a is the lattice constant that can be interpreted as the correlation length for local disorder in the case of independent single scattering events. It is found²⁷ that the maximum contribution to the sound attenuation coefficient α_{ph} is not due to thermal phonons, as in crystals without local disorder,²⁵ but long-wave phonons for which $\Gamma_{\text{ph},i}(k_{\text{ph}}) \approx \omega$, (where ω is the frequency of the sound)

$$\alpha'_{\text{ph}} = \frac{k_{\text{B}} T}{m_{\text{cell}} s^3} \frac{\omega}{(\Delta m_{\text{cell}}/m_{\text{cell}})^2 c(1-c)^{3/4}} \left(\frac{\hbar \omega}{T_{\text{D}}} \right)^{3/4}, \quad (12)$$

where T_{D} is the Debye temperature.

When both impurity and phonon scattering participate in establishing the disturbed equilibrium phonon distribution function, the main contribution to sound attenuation is due to phonons of frequency f_{ph} for which the two relaxation processes vary in phase, i.e., $\Gamma_{\text{ph,ph}}(f_{\text{ph}}) = \Gamma_{\text{ph},i}(f_{\text{ph}})$. At temperatures exceeding the Debye temperature²⁸

$$\alpha''_{\text{ph}} = \frac{\hbar \omega^2}{s k_{\text{B}} T} \left[\frac{k_{\text{B}} T}{m_{\text{cell}} s^2 (\Delta m_{\text{cell}}/m_{\text{cell}})^2 c(1-c)} \right]^{2/3} \quad (13)$$

We note by the way that if a particular phonon-impurity scattering remains while equilibrium is being established, then (12) will remain valid for $T > T_{\text{D}}$ as well.

The effect of local disorder on phonon attenuation of sound for shear waves at high temperatures can therefore be examined on the basis of either $\alpha'_{\text{ph}}(T)$ or $\alpha''_{\text{ph}}(T)$, since the sound attenuation coefficient is independent of temperature when equilibrium is established in the phonon subsystem

exclusively by phonon-phonon processes²⁵ for $T \gg T_{\text{D}}$. As far as frequency dependence is concerned, it does not appear to provide a great deal of information because, experimentally, it is difficult to distinguish between $\alpha_{\text{ph}} \sim \omega^2$ predicted by theory in the absence of disorder²⁵ and the expression $\alpha'_{\text{ph}} \sim \omega^{7/4}$.

From the methodological point of view, it is interesting to note that the formulas given by (12) and (13) can be obtained not as the imaginary part of the polarization operator, but from standard relaxation theory in the form of (5)–(8). In this approach, phonon attenuation of sound is due to an internal parameter in the system, which may be taken to be the phonon distribution function $\chi(f_{\text{ph}}, T)$ perturbed by the elastic wave. To calculate the attenuation coefficient we have to use the expression for the free energy in terms of $\chi(f_{\text{ph}}, T)$ and substitute it in (8). According to Ref. 31, the free energy of a crystal due to phonons is

$$F_{\text{ph}} = F_0 + k_{\text{B}} T \sum_r \ln \left[1 - \exp \left(- \frac{\hbar f_{\text{ph}}^{(r)}}{k_{\text{B}} T} \right) \right], \quad (14)$$

$$\chi(f_{\text{ph}}^{(r)}, T) = \left(\exp \frac{\hbar f_{\text{ph}}^{(r)}}{k_{\text{B}} T} - 1 \right)^{-1}, \quad (15)$$

where Σ_r represents summation over all the normal modes of the crystal. The disturbed equilibrium is restored in the r th mode by interactions with all other phonon modes. In traditional relaxation theory, the kinetics of the restoration of equilibrium is described by the relaxation equation given by (7) where the quantities $\delta \xi_{\text{ph}}^{(r)}$ are the differences between instantaneous and equilibrium value of the r th mode distribution function [Eq. (15)].

If we now express the free energy in terms of the distribution function given by (14) and (15) (this is the relaxation parameter), and substitute in (8), we obtain the sound attenuation coefficient and the change in the velocity of sound due to the establishment of equilibrium in the r th mode:

$$\alpha_{\text{ph}}^{(r)} \approx \frac{1}{2\rho s^3} \frac{k_{\text{B}} T}{\tilde{V} \chi^2(f_{\text{ph}}^{(r)}, T)} \left(\frac{\hbar f_{\text{ph}}^{(r)}}{k_{\text{B}} T} \right)^2 (\Lambda_{\text{ph}}^{(r)})^2 \frac{\omega^2 \tau_{\text{ph}}^{(r)}}{1 + \omega^2 (\tau_{\text{ph}}^{(r)})^2}, \quad (16)$$

where $\Lambda_{\text{ph}}^{(r)}$ is the deformation potential of the r th mode, $\tau_{\text{ph}}^{(r)}$ is the r th mode relaxation time constant, and \tilde{V} is the volume. Hence, if we consider that the contribution of the phonon modes are additive, the total sound attenuation coefficient in the elastic continuum approximation is found to be

$$\alpha'''_{\text{ph}} = \sum_r \alpha_{\text{ph}}^{(r)} = \frac{3\tilde{V}}{2\pi^2 s^3} \int_0^{\omega_{\text{D}}} \alpha_{\text{ph}}^{(r)2} f_{\text{ph}}^2 df_{\text{ph}}, \quad (17)$$

where \bar{s} is the average velocity of sound, given by

$$\frac{3}{\bar{s}^2} = \frac{2}{s_t^2} + \frac{1}{s_l^2},$$

in which s_t , s_l are the velocities of transverse and longitudinal waves, respectively, and ω_{D} is the Debye frequency. The specific dependence of α'''_{ph} on frequency and temperature is determined by the relaxation mechanism, i.e., by the dependence of $\tau_{\text{ph}}^{(r)}$ on the phonon frequency and the temperature. Thus, if $\tau_{\text{ph}}^{(r)}$ is independent of f , then the dependence of

α_{ph}''' on $\omega\tau_{ph}$ is purely relaxational. Conversely, if we use (11) for $\tau_{ph}^{(r)}$, then the integral in (17) can be evaluated between zero and infinity because the last factor in (16) falls very rapidly. For the same reason, long-wave phonons provide the main contribution to the integral. The integral then assumes a standard form³² and

$$\alpha_{ph}''' \approx \frac{3}{8\rho_s^3} (\bar{\Lambda}_{ph})^2 \left[\frac{\Delta m_{cell}}{m_{cell}} c(1-c) \right]^{-3/4} (s\alpha^3)^{-3/4} \omega^{7/4} k_B T. \quad (18)$$

It is readily shown that this expression is identical with (12), apart from some multiplying numerical factors. When a longitudinal deformation wave propagates through the medium, this also gives rise to a change in the local temperature that cannot relax to its equilibrium value (relative to the thermostat) by phonon-impurity scattering and normal processes in the phonon subsystem. Peierls³³ was the first to point out that umklapp processes have to be taken into account. The umklapp process was discussed in Ref. 34 in the absence of local disorder in the case where the umklapp time constant was much shorter than the time constants of normal processes. The opposite case was examined in Ref. 35. The emergence of the minimum characteristic time $\tau_{ph,i} = \Gamma_{ph,i}^{-1}$ in the problem, due to impurities, gives rise to a two-stage evolution of equilibrium.³⁶

The first to reach equilibrium, in a time τ_{1ph} , are the phonons corresponding to a particular constant-energy surface. We then have

$$\tau_{1ph}^{-1} = \tau_{ph,ph}^{-1} + \tau_{ph,i}^{-1}$$

because the contribution of the two processes is additive ($\tau_{ph,ph}^{-1} = \Gamma_{ph,ph}$). Phonon groups belonging to different constant-energy surfaces then reach equilibrium with one another because of phonon-phonon U -processes with characteristic time τ_{2ph} .

When $\tau_{2ph} \gg \tau_{ph,i}$, it is precisely the phonon-phonon processes that dominate the evolution of the overall equilibrium.

In the general case, the ratio of the contributions of different phonon-phonon and phonon-impurity processes to α_{ph} depends significantly on the kinetics of the local and the equilibrium temperatures. These questions have often been analyzed in the literature³⁷⁻⁴⁰ (see also Refs. 41-44), which means that shear waves are preferred in studies of local disorder effects. It is probable that it is precisely this situation that was encountered in experiments with longitudinal waves⁴⁵⁻⁵² in which doping had a significantly different effect as compared with shear waves.

In addition to the effects discussed above, there is also the influence of impurities on the phonon-phonon relaxation times⁵³ and on phonon-phonon correlation when the contributions of phonon modes to the overall attenuation coefficient are added together.⁵⁴

Local disorder can have a significant influence on the interaction of not only acoustic but optical phonons as well, which has a significant effect on the attenuation of sound in complex crystals with a large number of low-lying optical branches.^{38,55} They include rutile TiO₂ and aluminum yttrium garnets. In contrast to acoustic phonons, long-wave

phonons are unimportant in the scattering of optical phonons by impurities, and the main contribution is provided by phonon groups for which the density of states is high. Moreover, the contribution of optical-phonon scattering to the attenuation of sound depends not only on Δm_{cell} , but also on the position of the impurity in the crystal cell, which is in contrast to the case of acoustic phonons. Calculations⁵⁵ have shown that, in this case, α_{ph} is proportional to temperature and accounts for a fraction per optical branch of 0.1-1.0 of the sound attenuation coefficient per acoustic model.

An important feature of the attenuation of sound due to local disorder is its dependence on concentration. Since (11)-(13) are based on the Rayleigh scattering law, they are valid in a wide range of scatterer concentrations. This is so because, for randomly distributed impurities, the lattice constant is essentially the correlation length and estimates made in Ref. 28 show that (11) is also valid for $\Delta m_{cell}/m_{cell} \sim 1$ and $c \sim 0.5$.

This had led to attempts to apply this method to solid solutions as well, especially since, on the one hand, they are physically interesting because their concentration of disorder can be varied continuously within wide limits and, on the other, it may be possible to use them as a basis for new materials for high-frequency acoustic delay lines. For example, crystals of the solid solutions Zn_xCd_{1-x}Te have been investigated⁵⁶ at frequencies in the range 100-1 000 MHz and temperatures of 78-300 K for longitudinal, and for both fast and slow shear waves. Similar measurements have been made⁴⁰ on the solid solution Y_{3-x}Lu_xAl₅O₁₂ in the frequency range 0.5-5 GHz at temperatures between liquid helium and 80 K, and on Y_{1-x}Lu_xAl₅O₁₂ (Ref. 57).

These experiments have produced very interesting results that often do not fit the theory presented above although this theory does work qualitatively in a wide range of concentrations of local disorder and temperatures. It has been possible to provide a unified description of different types of temperature dependence.⁵⁶ For example, for shear waves, and in accordance with (12) and (13), the measured α increases with increasing T , although the increase is much slower for slow shear waves in CdTe and ZnTe, and there is a reduction for fast waves. On the other hand, a small peak has been found for longitudinal waves in Zn_{0.71}Cd_{0.29}Te at about 150 K, which has also been seen in CdTe and ZnTe separately.

A similarly complicated picture appears on the concentration and (especially) frequency dependence of the sound attenuation coefficient, although the overall trends remain. For example, the sound attenuation coefficient has a minimum as a function of the concentration of one of the components ($c \sim x$), as predicted by the theory. However, all the experimental functions show that the minimum of $\alpha_{ph}(x)$ is shifted away from $c = 0.5$. Thus, in Zn_xCd_{1-x}Te it is found⁵⁷ that $c_{min} \approx 0.7$, while in Y_{3-x}Lu_xAl₅O₁₂ the minimum is very broad and lies in the range $c = 0.2 - 0.35$ as x is varied.

For example, Fig. 1 shows $\alpha(x)$ for Cd_xZn_{1-x}Te, as reported in Ref. 56 for longitudinal and two shear waves (fast and slow). It is clear that the depth of the minimum is different for different types of wave. Thus, while for the fast shear wave the minimum of α is about 15 dB/cm, the figure for longitudinal waves amounts to a few dB/cm which corresponds to a reduction in the contribution of disorder due to

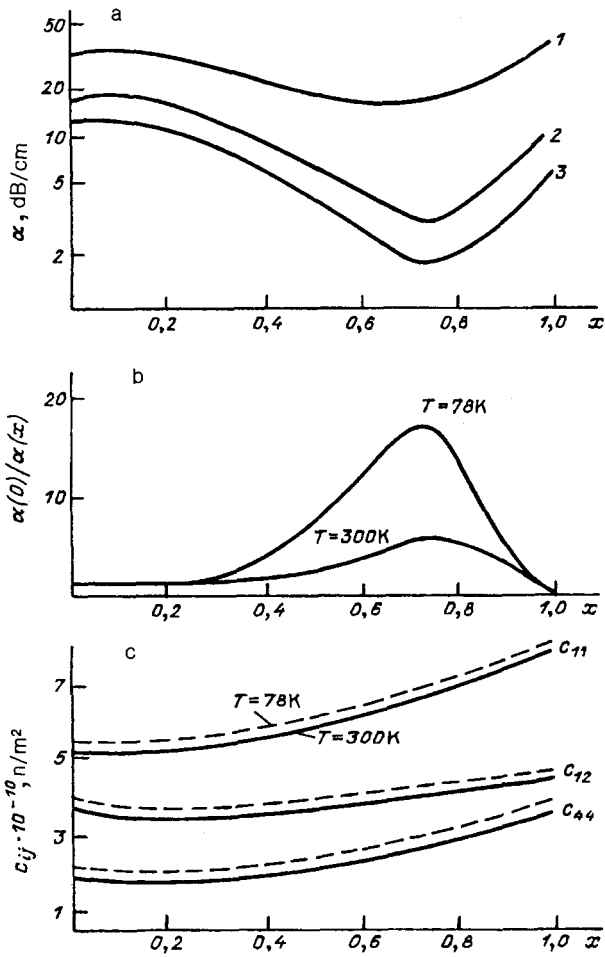


FIG. 1. Sound attenuation coefficient and elastic moduli of $\text{Cd}_x\text{Zn}_{1-x}\text{Te}$ as functions of concentration. a— $T=78\text{ K}$; 1—longitudinal waves, 2—slow shear waves, 3—fast shear waves; b—fast shear waves.

the higher velocity of sound against the background of temperature effects in the first approximation, which is independent of the concentration of disorder. It may be that cooperative effects have to be taken into account in solid solutions at high concentrations of disorder. This conclusion is supported by the temperature dependence of the above minimum:⁵⁶ its depth decreases with increasing temperature for the fast longitudinal wave (for example, at 300 K it is lower by a factor of 4 than at 78 K) and its position shifts toward higher x , which is in poor agreement with the ideas formulated for crystals with a random distribution of disorder. For shear waves, the attenuation α is controlled exclusively by the factor $c(1-c)$ which does not depend on temperature.

However, the greatest interest lies in the frequency dependence of the attenuation of longitudinal waves. It is found^{40,56} that the frequency dependence of α consists of two segments: at low frequencies the dependence is quadratic, whereas at high frequencies it is linear. The latter is ascribed in Refs. 40 and 56 to a manifestation of the Landau-Rumer mechanism, both because $\alpha_{\text{ph}} \sim \omega$ and because the temperature dependence of α_{ph} is found to be close to T^4 . However, the theory does not fit the fact that the transition from one mechanism to the other occurs abruptly, i.e., there is a break on the frequency dependence of α (Fig. 2 from Ref. 56). It is clear from Fig. 2 that in $\text{Zn}_{0.35}\text{Cd}_{0.65}\text{Te}$ at 300 K the

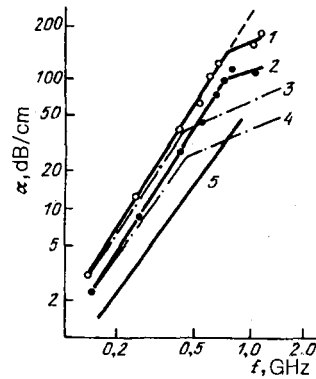


FIG. 2. Sound attenuation coefficient as a function of frequency. 1, 2, 5—300 K, 3, 4—78 K; 1, 3, 5— $x=0$, 2, 4— $x=0.35$; 1-4—longitudinal waves, 5—fast shear wave.

break occurs at about 800 MHz, whereas at 78 K it occurs at about 500 MHz for the same composition. It is also found⁴⁰ that the frequency at which the break occurs is a function of composition: for $\text{Y}_{2.7}\text{Lu}_{0.3}\text{Al}_5\text{O}_{12}$ the break occurs at 5 GHz whereas for $\text{Y}_1\text{Lu}_2\text{Al}_5\text{O}_{12}$ it occurs at 1 GHz.

However, it was shown in Ref. 42 that the Boltzmann transport equation could be used when sound attenuation was due to thermal phonons to calculate the sound attenuation coefficient for arbitrary $\omega\tau_{\text{ph,ph}}$, including $\omega\tau_{\text{ph,ph}} \ll 1$ (the Akhiezer case) and $\omega\tau_{\text{ph}} \gg 1$ (Landau-Rumer case). The formula obtained in Ref. 42 for α_{ph} contains a resonant term in the denominator, which is responsible for three-phonon processes with the corresponding selection rules, and a relaxation term responsible for the Akhiezer mechanism. Consequently, the transition from one mechanism to the other along the frequency axis is sufficiently smooth. It is possible that the break reported by the authors of Refs. 40 and 56 was simply due to the discrete selection of experimental frequencies, in which case the estimate for the point $\omega_c\tau_{\text{ph,ph}} \approx 1$ that characterizes the region of the change in the frequency $\alpha(f)$ is valid, and the dependence of ω_c on composition can be used to estimate $\tau_{\text{ph,ph}}(x)$, which was indeed done in Ref. 40.

We also note that the absence of a break for shear waves looks relatively strange within the framework of the standard method, although the study reported in Ref. 56 was carried out for different compositions in a wide range of frequencies.

If, however, the break on the frequency curve $\alpha(f)$ is abrupt, this is probably an indication that, for high enough concentrations of local disorder, the hypothesis of independent and randomly distributed Rayleigh scatterers begins to fail.

The sound attenuation coefficient was calculated in Ref. 58 for partially ordered mixed crystals. In contrast to the case of independent Rayleigh scatterers, the following three factors were taken into account: (1) a spatial fluctuations of concentration in the mixed crystals, (2) possible clusterization of the solid solution, and (3) the presence of long-range order elements.

In the first case, it was found that $\tau_{\text{ph,i}}^{-1}$ retained the concentration and frequency dependence. The second case had the same dependence on c and ω as the first, but the sound

attenuation coefficient was lower by the factor N_{cl} (the number of atoms per cluster) because the correlation function was higher by this factor.

In the third case, the Ornstein–Zernicke approximation and the assumption that the correlation length is less than the phonon mean free path together ensure that sound attenuation is as before determined by the phonon-phonon interaction. It is readily seen that the inclusion of correlations in the disposition of localized disorder has a significant effect on the sound attenuation coefficient and its concentration dependence, but it does not explain the abrupt change in the mechanism responsible for the interaction between sound and the phonon subsystem.

It is probable that an effective way to proceed would be to take into account the fact that, for high concentrations of disorder, weak and strong localization phenomena may arise in the phonon subsystem,^{59–61} so that an increase in concentration will be accompanied by, for example, the onset of clusterization phenomena or Gaussian fluctuations for which the spatial size of the most probable formations increases with increasing impurity concentration, which intensifies phonon scattering. This process exhibits the signs of a phase transition and leads to an abrupt increase in the phonon relaxation time because the diffusion coefficient tends to zero. The result of all this is that the frequency dependence of the sound attenuation coefficient changes from quadratic below the critical concentration to linear (in accordance with the condition $\omega\tau_{ph,ph} > 1$). The characteristic size of the scatterers is found to be of the order of the wavelength of sound, i.e., about 1 000 Å.

In accordance with experiment, the critical concentration is then different for different elastic-wave frequencies: for shorter waves the necessary characteristic cluster size is smaller, so that localization sets in for smaller x , which was indeed observed in Ref. 56.

2.1.2. We shall now examine an example of the direct contribution of local disorder to the acoustics of crystalline dielectrics. Since, as before, we shall be interested in long-wave acoustic oscillations, scattering effects will be insignificant and the elastic wave will act as a classical field but, in contrast to the preceding case, this field will act on the thermal motion of the units of local disorder themselves. These can be any one of: vacancies (Schottky and Frenkel' type), interstitial atoms and their complexes, individual impurity atoms that have entered the original crystal as it was being grown (or were introduced specially) and their complexes, complexes containing vacancies or interstitial atoms of the original crystal, and impurity atoms.

Local disorder produced in crystals as a result of intrinsic thermal motion in the crystal lattice will be called thermofluctuational, or simply thermal, and the other manifestations of local disorder will be referred to as nonthermal. The latter can be produced by doping, irradiation, and so on.

The difference between these two types of disorder as far as interactions with long-wave elastic waves are concerned is due to the fact that the equilibrium average concentration of thermal disorder, evaluated over the volume, is determined by temperature and mechanical stresses, and is therefore affected by the propagating wave, i.e., thermal defects can be annihilated and created.

At the same time, in the case of nonthermal disorder, its average concentration within the crystal volume always remains constant, and both strain and changes in temperature in the wave field produce a change in the local concentration and a corresponding redistribution of carriers of disorder in the crystal lattice over macroscopic (of the order of a wavelength) and microscopic (of the order of a lattice constant) distances. These differences lead to specific acoustic manifestations of both types of disorder.

Another important difference between local disorder of thermal and nonthermal origin is due to their significantly different temperature dependence, since the concentration of the former is a rapidly varying function of temperature whereas the concentration of the latter is practically constant (to within changes due to thermal expansion). Moreover, temperature has a considerable effect on the mobility of carriers of local disorder of both types and, consequently, on the characteristic times of the corresponding dissipative processes and the frequency range of elastic oscillations that are being effectively used.

It is thus clear that thermal disorder manifests particularly strongly at high temperatures because the necessary concentrations of 10^{-3} – 10^{-4} are reached for a temperature $T \approx T_D$ or higher. In this temperature range, the characteristic lifetimes of thermal defects are 10^{-6} – 10^{-7} s, which means that they are most readily observable in the long-wave part of the spectrum of ultrasonic oscillations.

Let us first consider the interaction between elastic waves and local disorder of thermal origin.^{18,24,63} Long-wave oscillations produce a deviation of the mean concentration of local disorder from its equilibrium value which, because of the establishment of equilibrium takes time, does not succeed in following the changes in strain and temperature in the wave field. This process can be described in terms of relaxation theory in which the equilibrium concentration of carriers of local thermal disorder is the effective internal relaxation parameter. We note, by the way, that in the linear approximation in the deviation from equilibrium, the thermal and diffusion fluxes of disorder produced by the elastic wave need not be taken into account because they are quadratic in strain and temperature.

To be specific, we shall consider that the carriers of local disorder in the crystal are Frenkel' vacancies with instantaneous concentration c . Since the concentration of carriers of local disorder is low until we reach the melting point, the free energy of a crystal containing local disorder can be calculated as the energy of a weak solid solution:³¹

$$F = F_0 + N_{i,t} k_B T \left(\ln \frac{N_{i,t}}{N_0} - 1 \right) + N_{i,t} \psi_t \quad (19)$$

where F_0 is the free energy of the crystal without disorder, $N_{i,t}$ is the number of Frenkel' vacancies, N_0 is the number of atoms of the original crystal per unit volume, and ψ_t is, in general, a certain function of temperature and mechanical stress. It can be shown that, for thermal defects, we may assume to a good approximation that $\psi_t = \text{const}$. Actually, if we assume that the interaction between vacancies can be neglected when

$$c_t = N_{i,t}/N_0 \ll 1$$

the equilibrium concentration that ensures minimum free

energy is proportional to $\exp(-\psi_i/k_B T)$. On the other hand, numerous experimental data on specific heats and volume expansion coefficients at high temperatures, from which it is not difficult to extract the contribution due to thermal defects,⁶³ suggest that the temperature dependence is of the form $\exp(-\text{const}/T)$.

In the case of deformed crystals, the expression given by (19) acquires an additional term due to the interaction between the elastic wave and local disorder, which takes the form $N_{i,t} E_{\text{int}}$ where E_{int} is the energy of interaction of a single point defect, given by⁶⁴

$$E_{\text{int}} = K\Omega_{ik}\mu_{ik}, \quad (20)$$

in which Ω_{ik} is a symmetric tensor describing the deformation of the lattice by a single carrier of local disorder of a particular type. The order-of-magnitude result is $\Omega_{ii} \approx a^3$ where for an interstitial atom $\Omega_{ii} > 0$ whereas for a vacancy $\Omega_{ii} < 0$.

If we evaluate the derivatives in (8) for the adiabatic propagation of elastic waves, we obtain

$$\alpha_{c,t} \approx \frac{c_t N_A}{2Ms^3 k_B T} \left(K\Omega_{ik} + \frac{k_B T \lambda_{ik,mm} \beta_{mm} \ln c_t}{C_V} \right)^2 \times \frac{\omega^2 \tau_{c,t}}{1 + \omega^2 \tau_{c,t}^2},$$

$$\frac{\Delta s_{c,t}}{s} = -\frac{\alpha_{c,t} s}{\omega^2 \tau_{c,t}^2}, \quad (21)$$

where M is the atomic weight and N_A is the Avogadro number.

The relaxation time for the process, $\tau_{c,t}$ and the equilibrium concentration of disorder, c_t , can be readily related to the creation and annihilation probabilities A_g and A_a for a carrier of thermal disorder by using standard equations.¹⁸ In the linear approximation,

$$c_t = A_g/A_a, \quad \tau_{c,t} = 1/A_a. \quad (22)$$

A number of points can be made about the probability of creation and annihilation of local thermal disorder. Since the creation and annihilation of local disorder requires the matched motion of a large number of atoms, the process is conveniently described phenomenologically in the multidimensional space of atomic configurations, each of which is characterized by its own potential energy.^{65,66} This model does not require a microscopic picture, and the frequency of creation of local disorder is calculated from the velocity of the imaging point between one potential minimum and another in the configuration space. The minima are separated by a saddle point on the $3N_A$ -dimensional surface that must be crossed by the imaging point, i.e., the height of the barrier that must be crossed in the transition from one state to the other must be equal to the difference V between the potential energies at the bottom and at the saddle point. Different configurations can be realized with probability proportional to the Boltzmann factor. Consequently,

$$A_g \sim \exp(-V_1/k_B T), \quad A_a \sim \exp(-V_2/k_B T). \quad (23)$$

Hence

$$c_t = c_t^* \exp\frac{V_2 - V_1}{k_B T}, \quad \tau_{c,t} = \tau_{c,t}^* \exp\frac{V_2}{k_B T}, \quad (23')$$

where c_t^* and $\tau_{c,t}^*$ are constants.

The exponential dependence of the equilibrium concentration of local disorder on the energy parameter can also be confirmed by thermodynamic calculations⁶⁷ if the variation of the free energy of the crystal with local disorder can be expressed in terms of the probability of realization of the state containing $N_{i,t}$ units of local disorder.

If we use combinatorial considerations to calculate the probability for the equilibrium concentration of defects that minimizes the free energy we again obtain (23').

The physical meaning of the pre-exponential factor in (23') is still not entirely clear. On the one hand, in the approach described in Refs. 65 and 66, $\tau_{c,t}^*$ can be interpreted as the effective frequency of attempts to overcome the potential barrier between one configuration and another. However, the numerical values of $\tau_{c,t}^*$ found from acoustic experiments for different crystals, lie in the range between 10^{-12} and 10^{-16} s, i.e., $(\tau_{c,t}^*)^{-1}$ is much greater than the limiting frequency of oscillations in crystal lattices, which is in poor agreement with the concept of effective frequency. It is possible that such low values of $\tau_{c,t}^*$ can be explained by recalling that they were deduced specifically from acoustic data, using the following condition for the observation of the relaxation maximum of $\alpha_{c,t}$ as a function of temperature at a particular frequency ω :

$$\omega \tau_{c,t}^* \exp(V_2/k_B T) = 1.$$

If $V_2 \neq \text{const}$ and decreases linearly and slowly with increasing T ($V_2 \gg k_B T$ up to the melting point), this must lead to a reduction in $\tau_{c,t}^*$. Of course, the value of V_2 found from the temperature shift of the relaxation maxima of α at different frequencies ω_1 and ω_2 , for which

$$\omega_1 \tau_{c,t}^* \exp(V_2(T_1)/k_B T_1) = \omega_2 \tau_{c,t}^* \exp(V_2(T_2)/k_B T_2),$$

turns out to be too low, but this is very difficult to establish by comparing V_2 calculated from acoustic data with values of V_2 found from measurements of transport coefficients (see below). As far as the reduction in V_2 with increasing temperature is concerned, one of the reasons for this may be the synchronization of the individual atomic motions due to anharmonism, since the latter gives rise to oscillation frequencies that exceed the limiting frequencies of collective modes in a given crystal lattice, and this generates individual oscillation modes.

Numerical calculations⁶⁸ have shown that, when an extended fluctuation is used to excite a chain of atoms for different pair interaction potentials, the phased collective motion of groups of atoms substantially reduces the threshold rupture energy. For example, when the chain is deformed by about one percent, the threshold energy is reduced by a factor of fifteen as we increase the number of excited atoms from two to ten.

Since for an elementary local disorder in the form of an interstitial-atom vacancy we have $\Omega_{ik} \approx \Omega_{ii}$, the orientational dependence of these effects is not well defined. It may be considered that it is precisely this mechanism that is responsible for the increase in the sound attenuation coefficient that has frequently been observed in different crystals for $T > T_D$, and is often referred to as the high-temperature

background (see for example, Refs. 23 and 69).

The most characteristic feature of the high-temperature background is its weak frequency dependence, revealed by measurements at frequencies in the range 10^5 – 10^6 Hz and above, and the monotonic increase with increasing temperature which is nearly exponential (Fig. 3).

In accordance with (21)–(23), and if the condition $\omega\tau_{c,t} \gg 1$ is satisfied, the temperature dependence of $\alpha_{c,t}$ is independent of frequency and is exclusively determined by the probability of creation of local disorder, i.e., $\exp(-V_1/k_B T)$. Measurements of the velocity of sound as a function of temperature, designed to reveal local disorder, are less informative because such data are masked by the temperature dependence of the elastic moduli, which is due to anharmonism.

The maximum of the sound attenuation coefficient as a function of temperature is observed when

$$\omega\tau_{c,t} = (2V_2 - V_1)/(V_1 + V_2) \quad (24)$$

which replaces the usual condition $\Omega\tau_{c,t} = 1$. Since direct methods have established that the concentration of thermal disorder increases with increasing temperature, the conclusion must be that $V_1 > V_2$. When $V_2 < V_1 < 2V_2$, acoustic experiments can reveal the maximum of the function $\alpha(T)$. On the other hand, for $V_1 > 2V_2$, we should observe an almost exponentially rising form of $\alpha(T)$ in the case of the modulation mechanism. In dielectrics, which usually have a high defect formation energy (as compared with $k_B T_m$), this mechanism leads to $\alpha_{c,t}(T, \omega)$ that is in agreement with the high-temperature background. Analysis of the data in Fig. 3 shows that $V_1 \approx 1$ eV in high-resistivity CdS.

Local disorder can manifest itself not only in the form of individual vacancies or interstitial atoms, but also in the form of elementary complexes, of which the simplest and most common is the complex consisting of a vacancy and an impurity atom. The above formulas for relaxational local disorder are then found to remain valid, but the process kinetics changes form because the probability that the complex will appear is determined by its lifetime and the specific mechanism of relative motion between the impurity and the vacancy. The strain produced by the elastic wave modulates the probability of creation (annihilation) of thermal local disorder, and modifies the equilibrium concentration of the complexes. When $\tau_{comp} > A^{-1}$ (τ_{comp} is the time necessary to produce the complex in the presence of the vacancy), the relaxational form of $\alpha(\omega)$ is preserved. However, in the op-

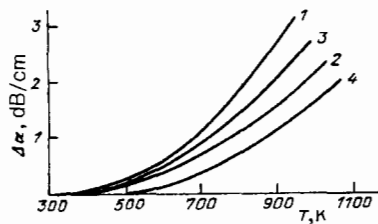


FIG. 3. High-temperature attenuation of sound in CdS at 15–75 MHz. 1, 2—high-resistance nonphotosensitive samples, 3, 4—low-resistance sample; 1, 2—longitudinal waves, 3—shear waves; 1, 3, 4—propagation along hexagonal axis.

posite limiting case, α has a specific frequency dependence that is often observed experimentally. When the point at which the vacancy occurs is not correlated with the position of the impurity, and the complex is formed as a result of the diffusion of the impurity toward the vacancy (because of the significantly different diffusion coefficient), the change in the concentration of the complexes in the acoustic field for $\omega > A_A$ is controlled not by the vacancy lifetime, but by the period t_s of the acoustic wave. The probability A_{comp} that a complex will be produced can then be calculated as the probability that the impurity will diffuse in a time $t < T_s$ over a distance of the order of the mean separation between the impurities, i.e., $N_i^{-1/3}$. If we describe diffusion in terms of uncorrelated one-dimensional hops, then we can show that⁷⁰ $A_{comp} \sim \omega^{-1/2} N_i^{2/3}$ if $\omega > D_i N_i^{2/3}$, i.e., the sound attenuation coefficient decreases with increasing frequency (D_i is the diffusion coefficient). This type of behavior of $\alpha_{c,t}$ has been frequently observed experimentally.²⁴ Thus, for $D_i \approx 10^6$ cm²/s, which is typical for high temperatures, and $N_i \approx 10^{-16}$ cm⁻³, $\alpha_{c,t} \sim \omega^{-1/2}$ for $\omega > 10^6$ Hz; for $D_i \approx 10^{-9}$ – 10^{-10} cm²/s (room temperature), this type of dependence is already observed for $\omega > 100$ Hz.

Let us now consider the interaction of long-wave elastic oscillations with nonthermal local disorder. The motion of carriers of local disorder is controlled by the chemical potential gradient, i.e., it occurs by spatial diffusion. In the simple case where the diffusion process does not involve several types of carriers of disorder (e.g., if we consider the motion of an impurity atom over the interstices), diffusion in the field of the elastic wave continues until chemical potential gradients of the crystal and the impurity become equal.

For more complicated types of motion of carriers of local disorder, when several types of carrier are involved (e.g., if we consider the motion of an impurity over vacancies), the perturbing force in the elastic wave field is due to gradients of chemical potential difference between impurity and vacancy, on the one hand, and the main lattice and vacancy, on the other. The sound attenuation coefficient $\alpha_{i,d}$ and the change $\Delta s_{i,d}$ in the velocity of sound can be calculated from the formulas

$$\alpha_{i,d} = \frac{c_{nt} K^2 N_A \Omega_{ik}^2}{M s^3 k_B T} \frac{\omega^2 \tau_{d,nt}}{1 + \omega^2 (\tau_{d,nt})^2}, \quad (25)$$

$$-\frac{\Delta s_{i,d}}{s} = \alpha_{i,d} \tau_{d,nt} s,$$

where c_{nt} is the concentration of nonthermal disorder and $\tau_{d,nt} = D_i/s^2$. Numerical estimates show that $\tau_{d,nt} \sim 10^{-16}$ – 10^{-18} s for diffusion coefficients in the range 10^{-6} – 10^{-8} cm²/s, i.e., this mechanism cannot be demonstrated experimentally in a direct way.

However, the situation changes if the crystal contains internal inhomogeneities that acts as sinks and sources for carriers of local disorder. These inhomogeneities can take the form of block boundaries, dislocations, and so on. Diffusion of carriers of local disorder, initiated by the chemical potential gradient produced by the elastic wave, continues over the distance to the nearest sink or source, which is much shorter than the wavelength λ of sound. To verify that the conditions for the experimental detection of the mechanism

are thus substantially improved, we rewrite $\tau_{d,nt}$ in the form $\tau_{d,nt} = 4\pi^2 D_i / \omega^2 \lambda^2$.

If we assume that diffusion takes place in the form of uncorrelated hops, the condition $\omega\tau_{d,nt} = 1$, i.e., the condition for the mechanism to be most effective, corresponds to the requirement that the carrier of local disorder has diffused to a distance λ during one wave period. If the separation between sources or sinks of disorder is $r_{dis} \ll \lambda$, we find that $\tau_{d,nt}$ is greater by the factor λ^2 / r_{dis}^2 . For example, for $D_i = 10^{-6}$ cm²/s and $r_{dis} = 10^{-6}$ cm, the condition $\omega\tau_{d,nt} = 1$ is satisfied for an elastic wave of 1 MHz.

Another source of interaction between elastic waves and local nonthermal disorder is the redistribution of its carriers within the unit cell due to the change in the position of their potential-energy minima in the deformed crystal lattice. This type of interaction has often been investigated for different types of local disorder (see, for example, the review given in Ref. 22). If it is possible to find r characteristic positions of local disorder in the unit cell, then each of these locations can be characterized by a strain tensor $\Omega_{ik}^{(p)}$ produced by a defect at the given point in the cell ($p = 1, 2, \dots, r$). If the carrier of local disorder is a single impurity atom, the symmetry of the tensor $\Omega_{ik}^{(p)}$ is determined by the symmetry of the position of the defect in the lattice. If, on the other hand, the carrier of local disorder is a set of several atoms with its own intrinsic symmetry elements, the symmetry of $\Omega_{ik}^{(p)}$ includes both the intrinsic symmetry of local disorder and the position symmetry.²²

We shall consider that the crystal contains an impurity in the form of r types of particle, and that when it is subjected to external deformation, its free energy must be rewritten in the form²⁴

$$F = F_0 + k_B T \sum_{p=1}^r c_{nt}^p N_0 (\ln c_{nt}^p - 1) + \sum_{p=1}^r c_{nt}^p N_0 \psi_p - \sum_{p=1}^r c_{nt}^p K \Omega_{ik}^{(p)} N_0 \quad (26)$$

where the last term represents the energy of interaction between the elastic wave and local disorder of type p . In the absence of deformation, the condition for minimum F when all the positions of local disorder in the cell are energetically equivalent yields

$$c_{nt}^p = c_{nt} / r,$$

where $c_{nt} = N_0 / N_A$ is the total concentration of local disorder.

The new equilibrium values of the concentration (c_{nt}^p)^e that reflect the redistribution of local disorder in the presence of the wave are found for

$$\sum_{p=1}^r c_{nt}^p = c_{nd} = \text{const}$$

from the condition for minimum F for each c_{nt}^p :

$$(c_{nt}^p)^e = \frac{c_{nt}}{r} \left[1 + \frac{K}{k_B T} \left(\Omega_{ik}^p - \frac{1}{r} \sum_{\rho=1}^r \Omega_{ik}^{(\rho)} \right) \right]. \quad (27)$$

Since all the displacements of the carriers of disorder occur within one or a few unit cells, i.e., $a \ll \lambda$, this can be

looked upon as a relaxation process, i.e., we have to take into account not the temporal but the spatial dispersion, and regard c_{nt}^p as the relaxation parameter. The sound attenuation coefficient due to the redistribution of the orientation of nonthermal local disorder is then given by^{22,24}

$$\alpha_{c,nt} = \frac{c_{nt} K^2 N_A}{2rs^3 k_B T M} \left[\sum_{p=1}^r (\Omega_{ik}^{(p)})^2 - \frac{1}{r} \left(\sum_{p=1}^r \Omega_{ik}^{(p)} \right)^2 \right] \frac{\omega^2 \tau_{nt}}{1 + \omega^2 \tau_{nt}^2}. \quad (28)$$

The characteristic feature of this sound attenuation mechanism is the strong anisotropy that distinguishes it from the modulational contribution of thermal disorder and enables us to classify the symmetry of local disorder²² on the basis of acoustic measurements. For example, in a cubic crystal, a shallow impurity atom produces local disorder of cubic symmetry, localized on the boundaries of the unit cell. Hence a plane elastic wave propagating along a space diagonal of the cube will not interact with this nonthermal local disorder. In general, the positional symmetry of local disorder should be lower than the symmetry of the unit cell in the crystal lattice.²²

The relaxation time τ_{nt} is determined by the frequency with which the potential barrier separating two impurity configurations within the unit cell is overcome by the thermal mechanism. In this sense, acoustic experiments provide us with a unique possibility of determining the characteristic cellular motion of carriers of disorder and, hence, the height of the potential barrier.

We note that comparisons of barrier heights found from acoustic data ($\omega\tau_{nt} = 1$) with those found from diffusion must be performed with some caution and must take account of the particular diffusion mechanism. If diffusion is due to the interstitial mechanism and takes the form of uncorrelated hops, the barrier height in the expression for the diffusion coefficient D_i is probably close to that determined from acoustic data. When diffusion involves the participation of vacancies, the diffusion and acoustic barriers turn out to be significantly different.

If the Ω_{ik} do not satisfy the conditions formulated above, the strain produced by the elastic wave is not accompanied by the displacement of carriers of local disorder, so that there is no contribution to the acoustic characteristics.

However, it is possible to use external factors, e.g., the imposition of a static mechanical strain that alters the symmetry of local disorder. For example, the effect of platinum and gold doping of silicon on the attenuation of sound was investigated in Ref. 71 where it was shown that the relaxation maxima of α appeared only when the samples were first subjected to mechanical treatment. The explanation given in Ref. 71 is based on the assumption that local disorder produces defects with orthorhombic symmetry and has six crystallographically equivalent orientations. Transitions between them can occur by tunneling, as in the case of Jahn-Teller centers. The result of this is that the effective symmetry of local disorder is raised to cubic symmetry, which removes all manifestation of relaxation in cubic crystals. On the other hand, mechanical strains give rise to anisotropy in the position of the centers, which reduces symmetry and gives rise to the attenuation of sound.

2.1.3. When carriers of disorder have nonzero electric charge, and the acoustic wave is accompanied by an electric field, this gives rise to processes that are analogous to those examined above, but do not require the corresponding symmetry of disorder.⁷² The physics of the phenomena is identical to thermal polarization of a dielectric⁷³ and reduces to the redistribution of localized disorder in the field of the elastic wave. Since these displacements occur on the scale of a few unit cells, i.e., $r_{\text{dis}} \ll \lambda$, the acoustic parameters can be calculated, as before, from relaxation theory.

The source of the electric field accompanying the elastic wave can be either the piezoelectric or the strain potential associated with local strain.

When the piezoelectric effect is present, the electric polarization due to the strain is⁷⁴

$$P_l = \beta_{lik} u_{ik}, \quad (29)$$

and the energy of interaction with a point defect with an effective charge q_{eff} is

$$E'_{\text{int}} = q_{\text{eff}} \beta_{lik} \varepsilon_{li}^{-1} u_{ik} \delta_m \equiv \chi_{ik}^{i,p} u_{ik}, \quad (30)$$

where β_{lik} is the piezoelectric tensor, ε_{lm} is the static permittivity tensor, and δ_m is the size of a hop in the direction of x_m .

The strain potential Λ_{ik}^d that produces the redistribution of the charged carriers of disorder in the unit cell under the influence of the electric field is related to the strain gradient within the cell, i.e.,

$$E'_{\text{int}} = q_{\text{eff}} \Lambda_{ik}^d (\partial u_{ik} / \partial x_m) \delta_m \equiv \chi_{ik}^d u_{ik}. \quad (31)$$

The electric field produced by the wave alters the probability of displacement of charged defects in the direction of the field.

The relaxation parameter ξ can be taken to the population difference between the directions along and against the field relative to some special plane:

$$\xi = (c_{q,ni})_2 - (c_{q,ni})_1 = \frac{c_{q,ni} E'_{\text{int}}}{1 + i\omega\tau_q},$$

where it is assumed that, in the absence of the wave,

$$(c_{q,ni})_1 = (c_{q,ni})_2 = \frac{1}{2} c_{q,ni}, \quad \tau_q = \tau_q^* \exp(V_2/k_B T).$$

Standard evaluations now yield the following expression for the sound attenuation coefficient due to charged carriers of disorder:⁷²

$$\alpha_{q,ni} = \frac{c_{q,ni} (\chi_{ik})^2 N_A}{2M_s^3 k_B T} \frac{\omega^2 \tau_q}{1 + \omega^2 \tau_q^2}, \quad (32)$$

where χ_{ik} must be replaced either with (30) or (31). If the carriers of local disorder have an intrinsic dipole moment P_{loc} , the formula given by (31) remains valid, except that we must now put $q_{\text{eff}} \delta_m = (P_{\text{loc}})_m$. We thus obtain the ultrasonic analog of thermal dielectric relaxation, and the characteristic time constants found from ultrasonic and electrical data are found to be equal. Of course, if the unit cell contains several potential-energy minima, this given rise to several

relaxation time constants and we have to sum over these constants in (31). Ultrasonic methods of finding $c_{q,ni}$ and τ_q may be found to be more effective than electrical methods when there is a danger that charge carriers may be injected from electrodes into the dielectric, and may affect the results.

2.2. Local disorder in crystalline semiconductors

The above mechanisms of local disorder in acoustic parameters operate, at least in principle, in crystalline semiconductors as well. The presence of mobile and localized carriers in the form of electrons and holes leads merely to a renormalization of numerical values of the variables that influence the attenuation coefficient and the dispersion of the velocity of sound. Thus, the electrons and holes can produce a change in the Grüneisen constant due to the components of the phonon spectrum, and there can be a change (due to the contribution of carriers to the free energy of the crystal) in the equilibrium velocity of sound. At the same time, diffusion of impurities and thermal defects is accompanied by transitions in the set of mobile and fixed carriers, and this produces a change in the activation energy for translational motion of carriers of local disorder, and so on.

In most experiments, local disorder is produced in semiconducting crystals by doping or by exposure to radiation. Semiconducting silicon and germanium, and also $A^{III}B^V$ and $A^{II}B^{VI}$ compounds have been investigated in particular detail (cf. the bibliography in Refs. 22, 24 and 71). Such measurements have revealed the presence of relaxation maxima on α as a function of frequency and temperature after doping with different impurities (Cu, B, Co, P, Fe, and so on). These data have been used to determine the activation energy for the relevant processes, whereas orientation properties have been used to establish the character of lattice distortions (type of carrier of local disorder).

We note that manifestations of local disorder of this type do not physically constitute a high-temperature phenomenon: an increase in temperature is accompanied by a reduction in the characteristic relaxation time of the relevant processes, which means that the frequency of the ultrasonic waves used in the experiments can be increased, so that the same (and not different) samples can be used to investigate the orientational dependence of α and Δ_s , which undoubtedly improves the reliability of the conclusions drawn from such data.

It has been found that the most characteristic types of local disorder are associated with the creation of complexes that include an impurity atom and dissolved oxygen atoms (more rarely, atoms of the host medium), and exhibit tetragonal or orthorhombic symmetry. The dependence of α on orientation and concentration shows that the mechanism responsible for attenuation of sound is reorientation of elastic dipoles in the field of the elastic wave, which was discussed above. The separation of the contribution of local disorder from the dislocational contribution, especially in elementary semiconductors, usually presents no difficulty because of the high quality of the crystals (dislocation density down to 10 cm^{-2}) although some experimental publications do not report the value of this parameter. Moreover, it is important to remember that the presence of dislocational disorder that cannot be controlled may have a significant distorting effect on experimental data for at least two reasons. First, impurity

atoms condensing on dislocations do not participate in the creation of elastic dipoles. Second, impurity atoms acting as pinning points for dislocations modify the length of the oscillating dislocation segments. This modifies the dislocational contribution to the attenuation of sound which is a complicated function of segment length, the parameters of the electronic and phonon subsystems, and frequency (see, for example, Refs. 20 and 23).

The contribution of the phonon deformation potential remains unaltered and increases linearly with temperature.

Mechanisms involving participation of local thermal disorder are specific to the high-temperature range. However, experiments and calculations have shown⁷⁰ that local thermal disorder is not differentiated with respect to the type of dielectric crystal, at least in elementary semiconductors, because of the high energy of formation of this disorder and, therefore, its low concentration up to temperatures approaching T_m .

Experiments and subsequent theoretical calculations have shown that mobile and localized carriers provide an additional contribution to the attenuation of sound in semiconductors. Here again we can distinguish two cases. If the main parameters of the interaction between the carriers and the elastic wave are functions of concentration, and of the character of local disorder, the contribution of crystalline local disorder to the parameters of the wave propagating through the electrons and holes is found to be mediated in accordance with the classification given above. If, on the other hand, the elastic wave produces a change in the characteristics of local disorder, which modifies the parameters of the electron subsystem, then we say that there is a direct interaction between disorder and sound.

The two types of interaction have significantly different effects in highly-doped and weakly-doped semiconductors. Strong and weak doping can be defined in terms of the degree of overlap of the electron states belonging to different impurities,^{74,75} and the corresponding conditions take the form $N_i r_B^3 \gg 1$ and $N_i r_B^3 \ll 1$, respectively, where r_B is the Bohr radius.

2.2.1. In highly-doped semiconductors, electrons have relatively high mobility and can therefore be regarded as essentially free. Even for relatively high rates of compensation d_k , the motion of carriers is not of the activation type. Since the Fermi energy ξ increases with the concentration of donor impurity N_{don} as $N_{\text{don}}^{2/3}$ (Ref. 74), whereas the energy of interaction of electrons increases much more slowly, i.e., only as $N_{\text{don}}^{1/3}$, the ideality of the electron gas increases with increasing local disorder in the absence of compensation, and the carriers themselves are distributed uniformly throughout the volume.

As the concentration N_{ac} of acceptor-type local disorder increases, i.e., as the degrees of compensation increases, the Fermi energy is found to decrease whereas the inhomogeneity of the distribution is of mobile carriers throughout the volume becomes greater, i.e., their concentration n_e becomes a function of position.

The attenuation of sound by free charge carrier was probably first calculated in Ref. 76 where it was assumed that the elastic wave perturbed the edges of the conduction and the valence bands through the electronic deformation

potential Λ^e . A spatially inhomogeneous distribution of carriers is produced as a result, but diffusion processes tend to smooth it out. The role of disorder in this analysis is thus seen to reduce to the effect on electron and hole lifetimes and, consequently, on the rate of inhomogeneity smoothing. It was subsequently found that a different mechanism was more effective in its contribution to the attenuation of sound in elemental semiconductors. It relies on the particular structure of the conduction band of silicon and germanium in which the deformation produced by the wave lifts the energy degeneracy; it produces a redistribution of electrons (holes) between the energy valleys and is characterized by a finite relaxation time $\tau_{e,d}$. Physically, the attenuation mechanism can be referred to as electron-deformational and constitutes an analog of the attenuation of sound by the redistributing elastic dipoles (see above), except that it occurs in energy space and can be calculated from the same formulas that give the result obtained by another method in Ref. 77 (the valley population difference is then the relaxation parameter), namely,

$$\alpha_{e,d} = \kappa_e \frac{n_e (\Lambda^e)^2 \omega^2 \tau_e}{2 \rho s^3 k_B T (1 + \omega^2 \tau_e^2)}, \quad (33)$$

where κ_e is a coefficient that depends on the wave type and the degree of carrier degeneracy.

Numerous early experiments with n-Ge and n-Si doped with group III and IV elements, and also the discussion of them, are described in Ref. 21. Later experiments are reported in Refs. 79–81. The numerical values of deformation potentials reported in different papers are in reasonable agreement and amount to 17.4 eV and 9.5 ± 0.7 eV for n-Ge (Ref. 21) and n-Si (Ref. 80), respectively. For p-Si, the data reported in Ref. 81 suggest that it is useful to introduce two electronic deformation constants, one of which is 1.2 eV and is due to the change in volume, whereas the other is 2.7 eV and is due to pure shear deformations.

In general, the relaxation time τ_e is given by

$$\tau_e^{-1} = \tau_{e,d}^{-1} + D_e (\omega/s)^2, \quad (34)$$

where D_e is the electron diffusion coefficient.

At frequencies below 1 GHz, the second term in (34) can be neglected. The intervalley relaxation time is then determined by three factors,²¹ namely, scattering by thermal phonons, by ionized impurities, and by neutral impurities. The corresponding time constants are $\tau_{e,ph} \sim T^{-3/2}$, and $\tau_{e,i} \sim T^{1/2}$, and $\tau_{e,ni}$, respectively. Scattering by neutral impurities is effective only at very low temperatures. The contribution of ionized donors is not through scattering by the Coulomb potential of the impurity, which is relatively ineffective, but through the process whereby electrons are captured from a valley by impurities, and are then released into another valley.⁸² Since local disorder manifests itself only through the last two terms, we readily see that intervalley electron relaxation is ineffective in studies of the role of disorder in semiconductors at sufficiently high temperatures (above 100 K). A detailed discussion of the temperature dependence and order-of-magnitude estimates can be found in Ref. 21.

At temperatures above 300–400 K, the electron-phonon deformational interaction cannot be observed be-

cause of the considerable reduction in $\tau_{e,d}$ and the masking effect of the phonon and phonon-impurity attenuation mechanisms.

Another type of mechanism that leads to energy loss in semiconductors is the perturbation of the spatial distribution of mobile carriers by the propagating wave. This perturbation can be produced either by a distortion of the band structure of the semiconductor⁸³ or by the electric field accompanying the elastic wave in piezosemiconductors.^{84,85}

Weinrich⁷⁶ has taken into account the modulation of the band gap ΔE_g by the propagating wave in the intrinsic semiconductor:

$$\Delta E_g = \lambda_{ik}^e \mu_{ik}. \quad (34')$$

In his description, the sound attenuation coefficient is gov-

$$M \equiv \frac{1 + \{[1 + l(\mu_e/\mu_p)]/\omega^2\tau_l\tau_{d,e}(1+l)\}}{1 + \{[1 + l(\mu_e/\mu_p)]/\omega^2\tau_l\tau_{d,e}(1+l)\} + i(1+l)[1 + l(\mu_e/\mu_p)]\omega\tau_{d,e}},$$

in which $l = n_e/p_e$ is the ratio of the equilibrium concentrations of mobile electrons and holes, μ_e and μ_p are the electron and hole mobilities, respectively, and $\tau_{d,e} = D_e/s^2$ is the characteristic time for the diffusion spreading of charge clouds, which is inversely proportional to the diffusion frequency $\omega_{d,e}$. At high temperatures, $T = 500$ – 600 K, the carrier lifetime in, for example, elemental semiconductors⁸⁶ is found to be 10^{-4} – 10^{-7} s and $\tau_{d,e} \approx 10^{-11}$ s. Hence, up to the megahertz frequency range, we have

$$\alpha_{e,E_g} = \frac{(\Lambda_{ik}^e)^2 n_e}{2\rho s^3 k_B T} \frac{\omega^2 \tau_l}{1 + \omega^2 \tau_l^2}. \quad (35')$$

A mechanism for the interaction between mobile charge carriers and an elastic wave was proposed in Ref. 70 and is analogous to that described above, except that it takes into account the doping properties of local disorder. It is known⁸⁷ that local thermal disorder in semiconductors distorts the original crystal lattice and produces additional local levels in the band gap. For example, acceptor type levels appear in the band gap of germanium and donor type levels in the band gap of silicon. The result of this is that, at high temperatures, the change in the concentration of mobile carriers, e.g., in n-type material, is due both to direct transitions from the valence band to the conduction band and to the influence of local thermal disorder (at such temperatures, the impurities that produce the nonthermal local disorder are usually all ionized). Under certain particular conditions, these effects can even lead to a change in the sign of carriers i.e., to the so-called thermal conversion. Ultrasonic oscillations that modulate the equilibrium concentration of thermal disorder are therefore capable of producing a perturbation of the equilibrium concentration of mobile charge carriers, which leads to the appearance of local currents in the conduction band, which are analogous to deformation currents, and to the attenuation of sound, which can be referred to as the electron-defect mechanism.

It was noted in Ref. 70 that the direct contribution of the modulation of thermal-disorder concentration to the at-

tened by the finite lifetime τ_l of the mobile carriers and by the diffusion of carriers due to the chemical potential gradient produced by the wave (see below). The attenuation coefficient is found by solving the set of equations that includes the wave equation and the continuity equations for the current and the electrostatic displacement vector, into which a self-consistent electric field has been introduced without using the Poisson equation, which ensures that the intrinsic semiconductor is electrically neutral.

The sound attenuation coefficient due to the electronic contribution is found to be

$$\alpha_{e,E_g} = -\frac{(\Lambda_{ik}^e)^2 n_e \omega}{2\rho s^3 k_B T(1+l)} \text{Im } M, \quad (35)$$

where

tenation of sound in dielectrics can be neglected because the energy of formation is high (2–3 eV) and, correspondingly, the concentration is low (10^{-6} – 10^{-7} cm⁻³) which amounts to about 0.01 dB/cm under optimum relaxation conditions.

The sound attenuation coefficient due to the electron-defect mechanism is calculated in Ref. 70. For example, for n-type semiconductors, it is given by

$$\alpha_{e,d} = \frac{(K\Omega_{ik})^2 n_e^T \omega}{2k_B T \rho s^3 (1+l)} \text{Im} \frac{M}{1 + i\omega\tau_{\text{comp}}}. \quad (36)$$

When $\omega\tau_{d,e} \ll 1$, $\omega\tau_l > 1$, and $\omega\tau_{\text{comp}} \sim 1$, this expression assumes the simpler form

$$\alpha_{e,d} \approx \frac{(K\Omega_{ik})^2 n_e^T}{2\rho s^3 k_B T(1+l)} \frac{\omega^2 \tau_{\text{comp}}}{1 + \omega^2 \tau_{\text{comp}}^2}, \quad (36')$$

where n_e^T is the equilibrium concentration of mobile carriers due to thermal disorder. For example, at high temperatures ($T \approx 600$ K) in germanium, for which the number of intrinsic band carriers n_e is much greater than the concentration N_{ac} of acceptors due to thermal disorder, the estimated n_e^T is $0.5N_{ac}$ at $T = 700$ K, while $n_e^T \approx 10^{19}$ cm⁻³ (Ref. 86) and $N_{ac} \approx 10^{18}$ cm⁻³. The estimates made for this temperature range are typical for practically all the semiconductors (of course, if we take account of the type of thermal levels produced by thermal disorder).

Numerical estimates of both contributions to sound attenuation in germanium show that, in the region of their maxima, they are of the same order of magnitude and amount up to ten dB/cm at a frequency of about 10^8 Hz (if we put $\Lambda^e = 17$ eV, $n_e = 10^{18}$ cm⁻³, $n_e^T = 10^{17}$ cm⁻³, $\Omega_{II} = 10^{-23}$ cm³). It follows that they are difficult to separate experimentally, especially if we recall that the carrier lifetime can be different for different samples, and it is quite

difficult to estimate the coefficient that relates the concentration of a particular type of thermal disorder to the number of thermal levels in the band.

The attenuation of sound was measured in Ref. 88 up to 1200 K in silicon and germanium at frequencies of 10^5 and 3×10^5 Hz, and the two maxima of α found for longitudinal waves propagating in the [111] direction were ascribed due to the deformational interaction in accordance with (35) (for the maximum at the lower temperature) and to the relaxation of dissolved oxygen atoms in accordance with (28). The fact that the maximum of α was observed at $T = 670$ K at the frequency of 10^5 Hz leads to the estimate 10^{-5} s for the relaxation time, and the temperature shift of the maximum can be used to show that the argument of the exponential during the relaxation time is about 1 eV.

Measurements of the attenuation of sound in germanium and silicon were also reported in Ref. 70, but for longitudinal and shear waves propagating in the [100] direction at the higher frequencies of 10^7 – 10^8 Hz. The samples used in these measurements had n-type and p-type conductivities with mobile carrier densities at room temperature in the range 10^{14} – 10^{17} cm^{-3} . The dislocation density of all the samples were determined on the surface and did not exceed 10 cm^{-2} , which meant that the dislocation contribution could be ignored.

The results of these measurements can be briefly summarized as follows (see also Fig. 4): (1) sound attenuation increases with increasing temperature, (2) the temperature dependence of the sound attenuation coefficient α does not depend on the type of ultrasonic wave or its direction of propagation, (3) the sound attenuation coefficient of silicon decreases with increasing frequency, and a similar tendency is observed in germanium, but is less well defined and there is no frequency dependence in the first approximation, (4) an increase in frequency is accompanied by a change in the temperature coefficient and in the temperature at which α begins to vary appreciably with temperature, and (5) the sign

of current carriers and the concentration of dopants have no effect (to within the experimental uncertainty) on the temperature coefficient of α , but they do influence the temperature at which α begins to increase appreciably; the influence of the dopants increases with decreasing frequency.

These results appear to demonstrate the considerable effectiveness of the electron-defect mechanism. Actually, the deformational interaction in silicon and germanium is significantly anisotropic because of the multivalley character of the conduction band (cf. Fig. 4). Moreover, the very slight effect of dopants is inconsistent with the mechanism in which the carrier lifetime acts as the relaxation time, especially since all the shallow impurities are found to be ionized in this temperature range.

Moreover, in the electron-defect mechanism, the orientational dependence of $\alpha_{e,d}$ is determined by the shape of the characteristic surface Ω_{ik} , which is probably nearly spherical for simple lattices. The slight effect of dopants can also be understood because, at sufficiently high temperatures, when the mechanism comes into its own, semiconductors such as silicon and germanium have intrinsic conductivities.

It may therefore be considered that the relaxation peaks observed in Ref. 88 are also due to the electron-defect attenuation, especially since the characteristic relaxation time is about 10^{-5} s and is in good agreement with the estimated lifetime of thermal defects at these temperatures.

The electron-defect interaction can also be used as a basis for an explanation of the specific frequency dependence of α in silicon, since it is known⁸⁷ that, in contrast to germanium, in which monovacancies are the source of thermal acceptor levels, the formation of thermal donor levels in silicon is associated with the creation of an impurity-vacancy complex. The resulting local thermal disorder in silicon cannot therefore immediately produce a thermal level in the band gap. The standard transport equation must then be modified in order to allow for the probability of formation of a thermal level during the lifetime of local disorder. If we

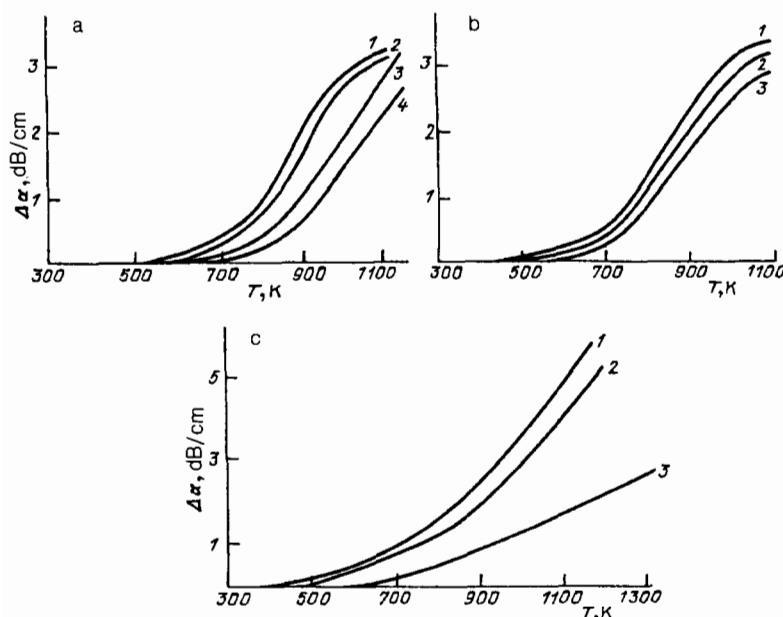


FIG. 4. Sound attenuation coefficient as a function of temperature for longitudinal waves in semiconductors. a—Ge. 1, 3—direction of propagation [111], 2, 4—direction of propagation [100]; 1, 2—15 MHz, 3, 4—85 MHz. b—Ge. 1— $n_0 = 1.8 \times 10^{14} \text{ cm}^{-3}$, 2— $p_0 = 1.7 \times 10^{14} \text{ cm}^{-3}$, 3— $p_0 = 10^{17} \text{ cm}^{-3}$; 15 MHz. c—Si. 1—15 MHz, 2—25 MHz, 3—55 MHz.

consider (a) that the characteristic time for the creation of the level is actually the time for the impurity atom to approach the thermal defect to a distance necessary for the creation of the complex, (b) that the transitional motion takes the form of correlated hops, and (c) that the disposition of the impurities is random, then according to Ref. 70 the frequency dependence of α is nearly exponential and depends on temperature.

The attenuation of sound at high temperatures, which has similar specific manifestations, has also been seen in non-piezoelectric directions in CdS samples with room-temperature conductivities of 10^{-8} – $10^{-2} \Omega^{-1} \text{cm}^{-1}$.

We note, by the way, that other manifestations of local disorder in semiconductors that are unrelated to local currents are found to be of minor significance. In particular, the change in the mean concentration of ionized carriers of local disorder that occurs in the field of the elastic wave provides, as does the change in the mean concentration of mobile charge carriers, the corresponding contribution to the free energy of the crystal, and may be looked upon as a relaxation variable in the spirit of the above discussion. However, the sound attenuation coefficient associated with this mechanism in, for example, silicon and germanium, is found to be small because of the local concentration of point defects, since whatever the depth of the energy level created by the point defect in the band gap, the dependence of the chemical potential on the concentration of free charge carriers excited into the conduction band (valence band) from the thermal levels can be written in the form $\sim \ln(Bc)$, which is the usual form for an impurity semiconductor (c is equal to the concentration of point defects when all the thermal levels are ionized and B is a slowly-varying function of temperature that, in the first approximation, is independent of deformation and carrier concentration) and α is determined by the derivatives of the chemical potential.

The longitudinal electric field E accompanying the elastic wave propagating in piezoelectric directions in piezosemiconductors produces a substantial perturbation of the electron subsystem. Piezoelectric directions in piezoelectric materials are defined as those in which the propagating elastic wave gives rise to an electric field with a well defined longitudinal component because the effective electron-elastic interaction is due to the tendency of, for example, the electron subsystem to screen off longitudinal electric fields.^{82–85} The efficacy of this interaction is much greater than that of the mechanism discussed above, which means that it can be exploited in studies of the properties of crystals exhibiting a slight piezoelectric effect.

The standard set of equations includes the wave equation, the equations of continuity for the current density j and the displacement $D^{(el)}$, and the corresponding expressions for the current density and displacement in the presence of the wave. The specific form of these equations depends on whether the particular semiconductor material is monopolar or bipolar.

For low concentrations of local disorder, its role reduces to the creation of local levels in the band gap, which behave as trapping or recombination centers. These questions are frequently being discussed in reviews and research publications in connection with the application of piezosemiconducting materials to the amplification of sound and the design of acousto electronic devices. A reasonably exten-

sive bibliography and a discussion of different aspects of this topic can be found, for example, in Refs. 24, 33, and 89–92.

Analogous problems have also been discussed for the interaction through the deformational potential in monopolar and bipolar impurity semiconductors with and without recombination and attachment centers (see, for example, Refs. 93 and 97). This interaction is much weaker in the long-wave range. Since there is a whole series of specific band structures in the presence of individual local disorder, it is very useful to have the general relation obtained in Ref. 97 by calculating the power released per unit volume per unit time (for the case where the concentration of field carriers is independent of position). By determining the crystal conductivity for different band gap structures, it is possible to obtain the sound attenuation coefficient in the form

$$\alpha_e = K_{EF}^2 \frac{1}{2s} \frac{\text{Re}(\sigma/\epsilon)}{[1 + \text{Im}(\sigma/\epsilon\omega)]^2 + [\text{Re}(\sigma/\epsilon\omega)]^2}, \quad (37)$$

where K_{EE} is the electron-elastic coupling coefficient that is readily expressed either in terms of the piezoelectric constant or the deformational interaction constant, σ is the electrical conductivity, and ϵ is the permittivity.

An increase in the concentration of local disorder in semiconductors may be accompanied by the appearance of a large-scale (as compared with the mean separation between carriers of disorder) potential due to fluctuations in the concentration of disorder. This potential is particularly significant when disorder is due to donor and acceptor impurities of similar concentration, i.e., when compensation takes place.^{74,75} As a result, the distribution of mobile charge carriers within the volume becomes inhomogeneous.

If we suppose that the carrier mean free path is much shorter than the typical dimensions of fluctuations, and the latter are much smaller than the wave length of the elastic wave, then we can use the hydrodynamic description. Moreover, the assumption that the mean free path of charge carriers is much shorter than the characteristic size of electrical inhomogeneities is equivalent to saying that the crystal has more efficient carrier scattering mechanisms that are unrelated to fluctuations, e.g., phonon mechanisms. This suggests that the mobility and the carrier diffusion coefficient may not be functions of position. In this approximation, the main set of equations describing the interaction between elastic waves and mobile charge carriers remains the same as in the homogeneous case, but the equations contain random functions of position, namely, the charge carrier concentration $n_e(\mathbf{r})$ and the random internal electric field $E_i(\mathbf{r})$, i.e., it is stochastic.

This problem was examined for n-type piezosemiconductors in different approximations in Refs. 98–101, since these effects had been investigated experimentally (see below) in some detail in the piezosemiconductors CdS and CdSe. The various formulas obtained are readily generalized to the case of interaction via the electronic deformation of potential on the assumption that the instantaneous (initiating) energy of interaction between the elastic wave and the mobile charge carriers in the case of the piezoelectric interaction is given by

$$U'_{\text{int}} = q_{\text{eff}} \int \beta_{ik,m} u_{ik} dx_m, \quad (38a)$$

and for the deformational interaction by

$$U''_{int} = \Lambda_{ik}^e u_{ik}, \quad (38b)$$

where q_{eff} is the effective charge of the carriers, x_m is the cartesian position coordinate, and $\beta_{ik,m}$ is the piezoelectric tensor.

If we can divide the piezoelectric field due to the piezoelectric elastic wave into two components, namely, the regular component $\langle E \rangle$ and the fluctuational component \tilde{E} with $\langle \tilde{E} \rangle = 0$, we can readily show that, since in real piezosemiconductors $(U''_{int})/(U''_w)^2 \approx K_{EE}^2 \ll 1$, the wave equation contains only $\langle E \rangle$:

$$\rho \partial^2 u / \partial t^2 = c_{33} \partial^2 u / \partial x_3^2 - \beta \partial \langle E \rangle / \partial x_3, \quad (39)$$

where U_w is the elastic energy of the propagating wave, u is the displacement in the wave, x_3 is the piezoelectric direction in the crystal, the wave equation is written in the form of a projection onto this direction, and $\langle \dots \rangle$ indicates statistical averaging over a volume that is large in comparison with the size of a fluctuation in concentration.

Different approaches are thus seen to differ by the approximation used to evaluate $\langle E \rangle$. For example, in Refs. 98 and 99, the sound attenuation coefficient is calculated by the effective medium method. The resulting expressions are relatively unwieldy, but become manageable in the approximation that is linear in $\langle \delta n_c^2 \rangle / \langle n_c \rangle^2 \ll 1$ and $\langle \delta n_c^2 \rangle = \langle (n_c - \langle n_c \rangle)^2 \rangle$ for $(r_{DH}/r_n)^2 \ll 1$, where r_{DH} is the Debye-Hückel screening and r_n is the characteristic size of inhomogeneities.

The main conclusion of these researches was the demonstration of the fact that the presence of inhomogeneities in the free-carrier distribution reduces the attenuation coefficient by an amount proportional to $\langle \delta n_c^2 \rangle / \langle n_c \rangle^2$. Moreover, it was shown that, when $\omega_{d,e} \gg \omega$, the frequency dependence of the sound attenuation coefficient was determined not by the mean electrical conductivity of the crystal, $\langle \sigma \rangle$, but by the effective conductivity σ_{eff} , defined by¹⁰²

$$\langle j \rangle = \sigma_{eff} \langle E \rangle. \quad (40)$$

For a compensated doped semiconductor¹⁰²

$$\sigma_{eff} = \sigma_0 \left(1 - \frac{1}{3} \frac{\langle \delta n_c^2 \rangle / \langle n_c \rangle^2}{1 - i\omega\tau_M} \right), \quad (41)$$

where σ_0 is the dc electric conductivity and τ_M is the Maxwellian time constant describing the spreading of a charge cloud and equal to ϵ/σ_0 .

Another approach was used in Ref. 100 in which a set of two rigorous equations was obtained for $\langle E \rangle$ and \tilde{E} , which was then solved approximately for typical special cases. For very small fluctuations for which $r_n^2 \ll \langle \tau_M \rangle D_e$, the sound attenuation coefficient was found to be

$$\alpha'_{e,n} = \frac{1}{2} \frac{K_{EE}^2}{s} \frac{\omega^2 \langle \tau_M \rangle (1 - b_1) / (1 + b_2)}{1 + [\omega^2 \langle \tau_M \rangle^2 (1 - b_1)^2 / (1 + b_2)^2]}, \quad (42)$$

where $b_1 = \mu_e^2 \Delta_E^2 l_E / D_e s$; and $b_2 = \Delta_n^2 l_n^2 / D_e \langle n_c \rangle^2 \langle \tau_M \rangle$, whereas the correlation functions for fluctuations in the internal electric field and in the concentration of carriers were assumed to be exponential:

$$\psi_E = \Delta_E^2 \exp(-r/l_E), \quad \psi_n = \Delta_n^2 \exp(-r/l_n),$$

where Δ_E , Δ_n , l_E , l_n are the variances and the correlation lengths of the corresponding quantities.

It is clear from (42) that, when small fluctuations are present, the condition for the detection of a maximum of $\alpha(\omega\tau_M)$ differs from that in the homogeneous case, but the height of the maximum remains the same.

When $b_1 \ll 1$ and $b_2 \ll 1$, the small correlation lengths ensure that (42) becomes identical with the expression for a homogeneous piezosemiconductor.⁸⁵

This situation arises in highly-doped uncompensated materials in which high carrier concentrations ensure that linear screening gives rise to Debye lengths that do not exceed a few dozen Å.

When the typical dimensions of fluctuations are sufficiently large, so that

$$D_e d^2 \tilde{E} / dx^2 \ll \tilde{E} / \langle \tau_M \rangle,$$

the sound attenuation coefficient is significantly different from the $n_c = \text{const}$ case:

$$\alpha'_{e,n} = \frac{1}{2} \frac{K_{EE}^2}{s} \frac{\omega^2 \langle \tau_M \rangle (1 - 2b_3 + b_4) / (1 + b_4)^2}{1 + [\omega^2 \langle \tau_M \rangle^2 (1 - b_4)^2 / (1 + b_4)^2]}, \quad (43)$$

where

$$b_3 = \mu_e^2 \Delta_E^2 s^{-2} [1 + (\omega^2 \langle \tau_M \rangle^2)^{-1}]^{-1},$$

$$b_4 = \frac{(\mu_e^2 \Delta_E^2 / s^2) - (\Delta_n^2 / \omega^2 \langle \tau_M \rangle^2 \langle n_c \rangle^2)}{1 + (\omega^2 \langle \tau_M \rangle^2)^{-1}}.$$

In contrast to the homogeneous distribution of carriers, the condition for maximum attenuation in the presence of a large-scale potential assumes the form

$$\omega \langle \tau_M \rangle = (1 + b_3) / (1 - b_4), \quad (44)$$

i.e., it may be shifted from $\omega \langle \tau_M \rangle = 1$ toward greater or smaller values of the dc conductivity. A study was also made of the possibility of amplification of sound by highly-doped piezosemiconductors using a constant drag field E_0 . It was found that sound amplification was possible when the dimensions of fluctuations in the internal field and the concentration of carriers were sufficiently small, but the necessary drag fields were somewhat stronger than $\mu E_0 = s$ (homogeneous case). When the dimensions of fluctuations are sufficiently large (this is the second condition), sound amplification may be very difficult to observe and a change in the sign of $\alpha'_{e,n}$ does not occur even when μE_0 is much greater than s .

An attempt to move on to larger inhomogeneities with $\omega r_n / s \lesssim 1$ was made in Ref. 101.

The principal result was the demonstration that, at least in the approximation in which $\langle \delta n_c^2 \rangle / \langle n_c \rangle^2 \ll 1$, the mean self-consistent electric field is as before expressed in terms of the longitudinal component of the high frequency effective conductivity $\sigma_{eff}^{\parallel}(\mathbf{k}, \omega, r_n)$:

$$\langle E \rangle = i\omega \beta u / (\sigma_{eff}^{\parallel} - i\omega \epsilon),$$

although geometric dispersion of σ_{eff}^{\parallel} is found to occur.

Substituting the last expression in (39), and performing standard operations, we obtain

$$\alpha''''_{e,n} = \frac{K_{EE}^2}{2s} \frac{\omega^2 \langle \tau_M \rangle [b_5 - (kR_1)^2]}{[\omega \langle \tau_M \rangle - (b_6 - kR_2)^2]^2 + [b_5 - (kR_1)^2]^2}, \quad (45)$$

$$b_5 = \operatorname{Re} \frac{\sigma_{\text{eff}}^{\parallel}(\omega, 0)}{\sigma(0)}, \quad b_6 = \operatorname{Im} \frac{\sigma_{\text{eff}}^{\parallel}(\omega, 0)}{\sigma(0)},$$

$$R_1^2 = \left(\frac{r_{\Pi}}{2} \right)^2 \cdot \frac{1}{15} \frac{1}{1 + \omega^2 \langle \tau_M \rangle^2} - r_{\text{dif}}^2 \frac{1 - \omega^2 \langle \tau_M \rangle^2}{(1 + \omega^2 \langle \tau_M \rangle^2)^2},$$

$$R_2^2 = \left(\frac{r_{\Pi}}{2} \right)^2 \cdot \frac{1}{15} \frac{\omega \langle \tau_M \rangle}{1 + \omega^2 \langle \tau_M \rangle^2} - r_{\text{dif}}^2 \frac{2\omega \langle \tau_M \rangle}{(1 + \omega^2 \langle \tau_M \rangle^2)^2},$$

$$\Delta s_{e,n} = \frac{K_{EE}}{2} s \frac{\omega \langle \tau_M \rangle [\omega \langle \tau_M \rangle - (b_6 - kR_2)^2]}{[\omega \langle \tau_M \rangle - (b_6 - kR_2)^2]^2 + [b_5 - (kR_1)^2]^2},$$

$$r_{\text{dif}}^2 = \frac{\varepsilon D_e}{\langle \sigma(0) \rangle},$$

and $\langle \sigma(0) \rangle$ is the mean dc conductivity.

Another approach for taking into account the influence of the large scale potential created by disorder fluctuations on the acoustic properties of a highly-doped semiconductor was proposed in Ref. 103 where static averaging over the volume was replaced with averaging over the energy E reckoned from the previous bottom of the conduction band (in the undoped crystal) on the basis of the ergodic hypothesis.¹⁰⁴

It is well known that many properties of highly-doped semiconductors can be successfully explained in terms of band bending.⁷⁴ This bending of the bottom of the conduction band is due to the spatial large-scale potential associated with concentration fluctuations, e.g., fluctuations in the concentration of donors in an n-type semiconductor. The root mean square random potential $\langle V \rangle$ and the radius R_{Π} of typical fluctuations can be estimated from the formula⁷⁴

$$\langle V \rangle = q_e N_1^{2/3} / \varepsilon n_e^{1/3}, \quad R_{\Pi} = N_1^{1/3} / n_e^{2/3}, \quad (46)$$

where N_1 is the total concentration of donors and acceptors. Hence it is clear that, as the mean concentration of disorder increases, and also as the degree of compensation increases, the range of changes in the large-scale potential increases and the bent bottom of the conduction band can cross the chemical potential ζ at a value equal to $m_{\xi} \langle V \rangle$ where m_{ξ} is a coefficient. Mobile carriers become localized in such regions and electron droplets arise in the n-type semiconductor. The attenuation of sound by electron droplets is discussed in Ref. 105.

In addition to localized carriers, the semiconductor also contains electrons that can participate in metal-type dc conduction (without activation). They occupy the percolation level E_{per} , i.e., they possess the minimum energy that electrons must have while moving on classically allowed trajectories in order to pass through a random potential distribution to infinite distance. Numerical calculations show that $E_{\text{per}} \approx m_{\xi} \langle V \rangle$ ($m_{\xi} < m_{\xi}$). In the first approximation, electrons at the percolation level behave as in a homogeneous sample although it is quite clear that, since the trajectory at the percolation level is quite complicated, the formation of electron bunches in the piezoelectric field is inhibited.

Highly-doped compensated semiconductors may therefore be considered, in the simplest case, to contain two sources of sound attenuation, namely, carriers at the percolation level and carriers localized in droplets.

Let us begin by considering the contribution of unlocalized charge carriers. In an arbitrary inhomogeneous case, we can combine the continuity equation for the displacement and the current, and take account of the constitutive relation of the piezoelectric medium. This yields the following equation for the self-consistent electric field E produced by the wave:

$$i\omega(\varepsilon E + \beta \frac{\partial^2 u}{\partial x_3^2}) = q_e \mu_e n_e(r) E + \frac{D_e \nabla_x n_e(r)}{4\pi n_e(r)} \nabla_x (\varepsilon E + \beta \frac{\partial^2 u}{\partial x_3^2}). \quad (47)$$

In general, the solution of (47) constitutes a relatively complicated problem (some special cases were discussed above). However, if the diffusion coefficient is small, or the gradients produced by charged inhomogeneities are such that the last term on the right hand side can be neglected, the sound attenuation coefficient depends only on $n_e(r)$, and averaging over the energies corresponding to all the possible impurity configurations can be readily carried out. For the Gaussian random potential distribution (see Refs. 74 and 103, and also Ref. 100), we find that

$$\alpha_{e,n}^{(IV)} = \frac{\omega k_B T}{\langle V \rangle} \frac{K_{EE}^2}{2s} \exp\left(-\frac{E_{\text{per}}^2}{\langle V \rangle^2}\right) \times \operatorname{arctg} \frac{\omega \tau_{\text{per}} \{\exp[(\sqrt{2}\langle V \rangle - E_{\text{per}})/k_B T] - 1\}}{1 + \omega^2 \tau_{\text{per}}^2 \exp[(\sqrt{2}\langle V \rangle - E_{\text{per}})/k_B T]}, \quad (48)$$

where

$$\tau_{\text{per}} = \frac{\varepsilon}{q_e \mu_e N_{\text{per}}} \exp[-(\zeta + E_{\text{per}})/k_B T],$$

in which τ_{per} , N_{per} are the relaxation time and the density of states at the percolation level, respectively. The expression given by (48) shows that inclusion of only the inhomogeneity in the electron density produces a significant reduction in the attenuation coefficient and alters the dependence of α on the frequency and conductivity if $\langle V \rangle / k_B T > 1$. Moreover, in contrast to the homogeneous semiconductor, a variation of frequency or electric conductivity produces different conditions for the observation of a maximum. When looked upon as a function of frequency, the attenuation coefficient α has a maximum for $\omega \tau_{\text{per}} = \exp(-\langle V \rangle / k_B T)$, whereas when it is regarded as a function of temperature, the condition is

$$\omega \tau_{\text{per}} = \left(1 + \frac{2,1\langle V \rangle}{E_{\text{per}} - \zeta} - \zeta\right)^{1/2} \exp\left(-\frac{E_{\text{per}} - \zeta + 2,1\langle V \rangle}{2k_B T}\right). \quad (49)$$

It is clear from this expression that, in a semiconductor with a random large-scale potential, the change in α due to a change in temperature or in radiance on a photosensitive sample produces significantly different results. By measur-

ing α at several frequencies up to the maximum of α , it is possible to obtain an estimate for the root mean square value of the random potential.

Let us now consider the attenuation of sound by carriers localized in droplets.¹⁰⁵ When droplets are present, it is essential to take into account their polarizability P_{dr} in the piezoelectric field of the wave. According to Ref. 106, the polarizability P_{dr} of a spherical droplet of volume \tilde{V}_{dr} , containing charges q_{dr} with concentration $n_{e,dr}$ and mobility $\mu_{e,dr}$, is given by

$$P_{dr} = i\epsilon \frac{\sigma_{dr}/\omega}{3\epsilon + (i\sigma_{dr}/\omega)}, \quad \sigma_{dr} = q_{dr}\mu_{e,dr}n_{e,dr}$$

and the polarization vector p_{dr} is

$$p_{dr} = \tilde{V}_{dr}(n_{e,dr}/n_{e,per})P_{dr}E.$$

If we consider that all the droplets have the same localized-carrier density, then standard calculation of the sound attenuation coefficient¹⁰⁵ gives

$$\alpha_{e,dr} = \frac{K_{EE}^2 \langle n_{e,dr} \rangle}{2s n_{e,dr}} \frac{\omega^2 \tau_{dr}}{1 + \omega^2 \tau_{dr}^2}, \quad \tau_{dr} = \frac{3\epsilon}{\sigma_{dr}}, \quad (50)$$

where $\langle n_{e,dr} \rangle$ is the mean density of electrons localized in the droplets ($\langle n_{e,dr} \rangle + \langle n_{e,per} \rangle = \langle n_e \rangle$, $\langle n_{e,per} \rangle$ is the mean density of electrons at the percolation level). Hence it is clear that acoustic measurements, especially those performed at low temperatures, when the concentration of electrons at the percolation level is low, can serve as an effective tool for finding the parameters of electron droplets without depositing electrons on the sample. Thus, for $\omega\tau_{dr} = 1$, $\langle n_{e,dr} \rangle/n_{e,dr} = 0.01$, and the frequency of 10^9 Hz, the sound attenuation coefficient is $\alpha \approx 30$ dB/cm. We note that an analogous energy attenuation mechanism operates in the case of microwave measurements.¹⁰²

In a compensated highly-doped real semiconductor, the concentrations of localized carriers in droplets are significantly different. This means that we have to average over $n_{e,dr}$ in (50) because this quantity depends on the droplet size. If we suppose that the well-depth distribution function is Gaussian, we can express the well radius in terms of its depth¹⁰⁷ and take the average. Like (47), the resulting formulas contain $\arctan(\omega\tau_{dr})$, which for narrow distributions takes the form of the relaxation function. Two factors, noted in Ref. 107, must be borne in mind when we investigate the temperature dependence of the sound attenuation coefficient. First, the degenerate state of electrons in a droplet becomes nondegenerate at higher temperatures. For example, estimates made in Ref. 107 show that, in n-InSb with $n_e \approx 10^{15} \text{ cm}^{-3}$, the degeneracy temperature is about 30 K. Second, the well radius and, hence, the carrier concentration in the droplet are functions of temperature. For example, for a well depth of about $k_B T$, the droplet radius is proportional to T^2 . At higher temperatures, the rise in the droplet radius is slower. Moreover, it was noted in Ref. 107 that an increase in temperature is accompanied by an increase in the activation energy which has to be supplied to take the droplet electrons to the percolation level, which changes the time necessary to

establish equilibrium between the percolation level and the droplets.

At intermediate temperatures, and in the first approximation, the measured sound attenuation coefficient should be the sum of the contributions given by (48) and (50).

However, we must remember that, when electron droplets are present and the temperatures are finite, there is a definite probability of a thermal transition of electrons from droplets to the percolation level, which results in vacancies in the droplets, so that they behave like multiply-charged centers.

In the electron cloud produced at the percolation level in an n-type semiconductor, only a fraction f_e is found to be mobile because some of the electrons in the cloud are trapped by droplets and for a time $\tau_{per,dr}$ leave the cloud for the percolation level. These processes are analogous to the effect of traps on sound attenuation (see the bibliography in Ref. 24), so that the sound attenuation coefficient due to electrons at the percolation level can be calculated from the formula obtained in Ref. 108 for a homogeneous semiconductor containing attachment centers:

$$\alpha_{e,n}^{(v)} = \frac{K_{EE}^2 \omega}{2s} \times [\omega\langle\tau_M\rangle + a_1(a_2 f_e \omega^2 \langle\tau_M\rangle \tau_{d,e} + a_1 \omega \langle\tau_M\rangle)] \times [(\omega\langle\tau_M\rangle - a_1)^2 + (1 + a_2 f_e \omega^2 \langle\tau_M\rangle \tau_{d,e} + \omega \langle\tau_M\rangle a_1)^2]^{-1}, \quad (51)$$

where

$$a_1 = \frac{\omega\tau_{per,dr}(1-f_e)}{f_e + \omega^2\tau_{per,dr}^2}, \quad a_2 = \frac{f_e^2 + \omega^2\tau_{per,dr}^2}{f_e(f_0 + \omega^2\tau_{per,dr}^2)}, \quad \tau_{d,e} = \omega_{d,e}^{-1}$$

Here it is important to emphasize that the effect of trapping processes in inhomogeneous semiconductors is stronger than in the homogeneous material because $n_{e,k}$ is different in different droplets and the droplets have a size distribution. The spatial gradient of electron density is therefore determined not by the wavelength of sound, but by the droplet separation l_{dr} , so that $\tau_{d,e}$ is estimated to be $4\pi^2 D_e / \omega^2 l_{dr}^2$ which increases $\tau_{d,e}$ by the factor λ / l_{dr} .

The result of this is that the attenuation coefficient due to electrons at the percolation level is reduced even more in comparison with the homogeneous case.

Another model of disorder in piezosemiconductors is investigated in Refs. 109 and 110 in which it is assumed that the disorder takes the form of alternating layers with different electrical conductivity. It is well known¹¹¹ that, in this configuration, the electrostatic displacement must satisfy boundary conditions for discontinuous changes in σ , which results in a net surface charge on the separation boundaries, so that a polarization relaxation process is observed when there is a change in the sign of the external alternating electric field accompanying the elastic wave. The result is a change in the attenuation coefficient for the piezoactive wave, and also a change in the position of the maximum of the attenuation coefficient α . The weak point of this model is the requirement of a discontinuous change in σ because the smoother the transition from one region to another, the

smaller the effect. In natural materials, such boundaries probably accompany twinning because it is difficult to imagine that they occur across the boundaries of fluctuational inhomogeneities.

The effect of disorder on the attenuation of sound was demonstrated in Ref. 112 and was subsequently investigated in Refs. 103 and 113–115 although the possible uncontrollable manifestation of microinhomogeneities had frequently been reported before.^{116–118}

The attenuation of sound in piezoactive directions was investigated in Ref. 112 for longitudinal and shear waves in cadmium sulfide, highly-doped with copper ($c = 10^{-3}$), in which the concentration of mobile carriers and, hence, the dc electrical conductivity were regulated either by illumination or by temperature. It was established that, despite the fact that the condition $\omega\langle\tau_M\rangle = 1$ was definitely satisfied, and the effect of trapping levels was absent (because of the particular frequency at which the measurements were taken), the attenuation maxima were not observed, as predicted by the theory constructed for homogeneous samples.^{84,85}

These experiments were continued in Refs. 112 and 113 and also in Refs. 114 and 115. The sound attenuation coefficient was measured in Ref. 102 for longitudinal and shear waves at frequencies in the range 10^7 – 10^8 Hz in single-crystal cadmium sulfide and selenide. The condition $\omega\tau_{d,e} \ll 1$ was easily satisfied ($\tau_{d,e} \approx 10^{-10}$ s), which meant that trapping levels due to local disorder had no effect on these measurements. The dark conductivity of the CdS samples was 10^{-7} – $10^{-10} \Omega^{-1} \text{cm}^{-1}$, whereas the corresponding figures for CdSe were 10^{-8} – $10^{-9} \Omega^{-1} \text{cm}^{-1}$. The conductivity was increased to $10^{-3} \Omega^{-1}$ by varying the illumination, which ensured that $\omega\langle\tau_M\rangle$ could be varied in the range $\omega\langle\tau_M\rangle \ll 1$ to $\omega\langle\tau_M\rangle \gg 1$. Variation of temperature in the range 300–900 K was used to vary σ and hence, $\omega\langle\tau_M\rangle$.

Measurements showed that there was a large batch of samples for which the maximum of α was observed for longitudinal and shear waves propagating in piezoactive directions, but the position of the maxima on the σ scale for $\omega = \text{const}$ was a rapidly varying function of the method used to vary σ (by illumination or temperature Fig. 5). More-

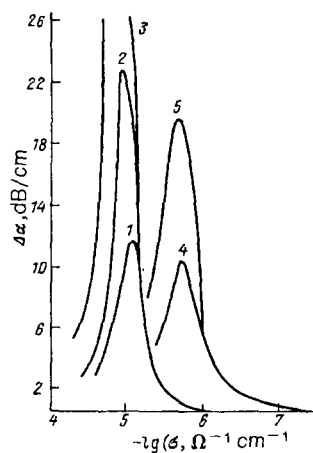


FIG. 5. Sound attenuation coefficient of photosensitive CdS as a function of conductivity. 1–3— σ varied by varying temperature, 4, 5— σ varied by varying illumination, 1, 4—15 MHz, 2, 5—2.5 MHz, 3—55 MHz.

over, there was a batch of samples in which variation of σ by illumination did not produce the maximum of α for either longitudinal or shear waves although the necessary condition for homogeneous samples, $\omega\langle\tau_M\rangle = 1$, was satisfied. At the same time, the maxima of α were observed by varying the temperature, but not for $\omega\langle\tau_M\rangle \approx 1$ (Fig. 6).

Measurements of $\sigma(\omega)$ also showed a strong dependence on frequency although, obviously, the frequencies involved in these measurements were much lower than the relaxation frequencies of the electron pulses. The variance of electrical conductivity decreases with increasing temperature and vanishes altogether at temperatures in the range 600–700 K. All these experimental results can be interpreted in the spirit of the above theory as a manifestation of the large-scale potential, since the microscopic homogeneity of the samples was monitored by the electric-probe method. The internal electric field introduced by local disorder produces a dephasing of the electron clouds produced under the influence of the piezoelectric field of the elastic wave. Accordingly, and in contrast to the homogeneous case, the attenuation of sound is no longer characterized unambiguously by the time constants $\langle\tau_M\rangle$ and $\tau_{d,e}$, and the function $\alpha(\sigma)$ ceases to have extrema, i.e., the piezoelectric attenuation of sound by mobile carriers is not readily detected experimentally.

The long-term relaxation of photoconductivity observed in these samples is also an indirect confirmation of their microinhomogeneity, since, in accordance with Refs. 119 and 120, the large-scale potential prevents the recombination of photoexcited carriers and increases the relaxation time.

The general properties of photoabsorption of sound by inhomogeneous piezosemiconductors are discussed in Ref. 24.

Measurements of the piezoactive sound attenuation coefficient of CdS and CdSe are discussed in Ref. 115 where it is reported that the measured photoabsorption of sound is not in agreement with the theory of homogeneous materials, and comparisons are with direct observations of structure, performed with an electron microanalyzer. A correlation is

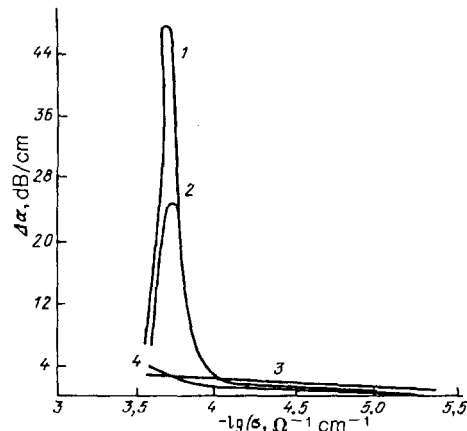


FIG. 6. Same as Fig. 5. 1, 2, 4— σ varied by varying temperature, 3— σ varied by varying illumination, 1 and 2, 3—piezoactive direction of propagation, 55 MHz and 25 MHz, respectively, 4—nonpiezoactive direction of propagation, 25 MHz.

established between these acoustic effects and surface impurity clusters. In samples in which the departure from the homogeneous-sample theory did not exceed 30–40%, the surface cluster density reached 10^3 cm^{-2} . It was also noted in Ref. 115 that samples with greater manifestations of inhomogeneity had an anomalously high real part of permittivity at the frequency of the ultrasonic wave.

The contribution of electron droplets to the measured sound attenuation coefficient is relatively difficult to determine experimentally. The principal criterion is probably the loss of metallic conductivity when the strong doping condition is satisfied at low temperatures and for strong compensation. It will be shown later that the photosensitivity of sound attenuation and the absence of dc conductivity are in themselves insufficient for the unambiguous identification of the contribution of electrons localized in droplets to the attenuation of sound because the same experimental effect is produced by weak doping and strong compensation. Acoustic experiments in a magnetic field may be very useful in this connection because, in the case of weak doping, the external magnetic field deforms the electron wave function on a donor and, as has been shown by Gal'perin *et al.*,¹²¹ this leads to a nonmonotonic function $\alpha(\mathbf{H})$. On the other hand, $\sigma_{\text{eff}} \sim H^{-2}$ in the case of metal type conductivity. Unfortunately, this magnetic-field dependence is strictly valid only for homogeneous materials. The form of $\alpha(\mathbf{H})$ changes when there are gradients of the concentration of mobile carriers, but it remains monotonic. The deviation from $\sigma_{\text{eff}} \sim H^{-2}$ was used in Ref. 118 to conclude that microinhomogeneities contributed to the attenuation of sound.

The various interactions of elastic waves with donor and acceptor disorder discussed above have not yielded an explanation of the entire range of experimental data now available.

Figure 7 shows the measured sound absorption coefficient of single-crystal CdS containing local disorder in the form of copper atoms, acting as acceptors, as a function of concentration. These results were obtained by spectral methods for concentrations of the order of 10^{-3} (Ref. 112).

It is clear from Fig. 7a that, for longitudinal waves, the attenuation of sound in a piezoactive direction exhibits a maximum that is entirely absent in the case of piezoactive shear waves. This is in conflict with the different mechanisms discussed above because, if it is the piezoelectric field that perturbs the electronic subsystem, there should be no difference between measurements on piezoactive longitudinal and shear waves (except for the trivial manifestations of

the difference between the propagation velocities). The experiments reported in Ref. 112 show that the interaction is anisotropic and well defined only for longitudinal waves propagating along the hexagonal axis (which is also a piezoactive direction), suggesting that the corresponding mechanism is due, on the one hand, to a change in volume and, on the other hand, to the piezoelectric interaction. The interaction is sensitive to the concentration of mobile carriers, since the variation of conductivity by variation of illumination reveals a maximum of α for longitudinal waves at constant temperature (Fig. 7). There is no photoabsorption in the case of shear waves.

The results reported in Ref. 112 are confirmed in Ref. 115 where it is also noted that one particular batch of samples showed a significant difference between the attenuation of longitudinal and shear piezoactive waves. A low concentration of surface impurity clusters of up to 10^6 cm^{-2} was observed optically for the same samples.

It may be considered that, because of the large fluctuations in point-defect concentration, the concentration of mobile charge carriers is significantly inhomogeneous which, as was shown above, smears out the electron clouds produced by the piezoelectric field and turns off the attenuation mechanism. However, because of the presence of large (dimensions amounting to dozens of Å) fluctuations in the concentration of local disorder, a new sound attenuation mechanism is found to appear. It relies on the deformational change produced by the longitudinal wave in the concentration of carriers of disorder (donors and acceptors) in a fluctuation, i.e., a change in its polarization. Since these fluctuations are immersed in the electron liquid, the change in electrostatic displacement is accompanied by a redistribution of the mobile carriers that screen the fluctuation.

If we suppose that the fluctuations are Gaussian, and take the form of a sphere of radius R_{fl} , the change in the displacement of one mean square fluctuation is of the order of

$$\delta P_{\text{fl},1} = \frac{q_{\text{dis}}(N_{\text{fl}}R_{\text{fl}}^3)^{1/2}}{4\pi\epsilon R_{\text{fl}}^2} u_{ii} = \frac{q_{\text{dis}}N_{\text{fl}}^{1/2}u_{ii}}{4\pi\epsilon(R_{\text{fl}})^{1/2}},$$

where u_{ii} is the change in volume in the wave and q_{dis} is the charge on a carrier of local disorder. Correspondingly, the estimated total change in the polarization of the volume is

$$\delta P_{\text{fl}} = N_{\text{fl}} \tilde{V} \delta P_{\text{fl},1},$$

where N_{fl} is the number of fluctuations per unit volume and,

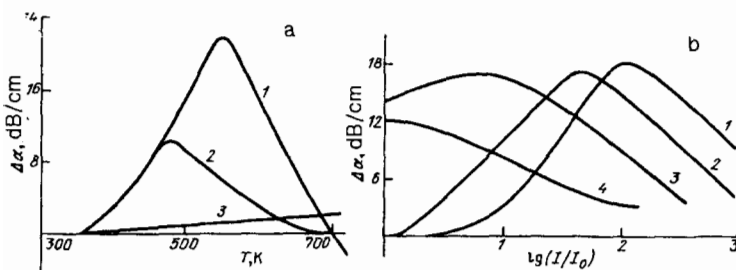


FIG. 7. Same as Fig. 5 for CdS + Cu. a: 1, 2—longitudinal waves, 3—shear waves in piezoactive directions, 1—75 MHz, 2—25 MHz, 3—15–75 MHz. b: 1—300 K, 2—450 K, 3—530 K, 4—610 K; I_0 —illumination at the beginning of changes in α .

for the sake of simplicity, all the fluctuations are assumed to have the same optimum radius. By repeating the discussion given in Ref. 74, we reach the conclusion that the maximum contribution to α in the absence of correlations is provided by fluctuations of radius equal to the Debye-Hückel length. Standard operations then show that the sound attenuation coefficient due to the piezofluctuational interaction is given by

$$\alpha_{p,\Pi} \approx \frac{\beta q_{\text{dis}} \bar{V} N_1^{1/2} N_{\Pi} R_{\Pi}^{-1/2}}{2\epsilon \rho_s^3} \frac{\omega^2 \langle \tau_M \rangle}{1 + \omega^2 \langle \tau_M \rangle^2}. \quad (52)$$

We note that the attenuation of sound by the above mechanism occurs only near each fluctuation and is unrelated to the motion of mobile carriers due to their chemical potential gradient created by a deformation in the wave. Inhomogeneities in the distribution of charged carriers due to the large-scale potential have practically no effect on this mechanism which continues to operate despite the removal of the usual (see above) gradient mechanism of piezoelectron interaction. Of course, if we take into account the size distribution of the fluctuations around the optimum value, we obtain

$$\alpha'_{p,\Pi} = \langle \alpha_{p,\Pi} \rangle,$$

which produces a broader distribution $\alpha'_{p,\Pi}(\omega \tau_M)$ as compared with the Debye case. This is in agreement with experiment (see Figs. 5–7). At the same time, numerical estimates of $\alpha_{p,\Pi}$, can be readily deduced from the data reported in Ref. 115 rather than from the mobile-carrier concentration which is not accurately known. If we take the number of fluctuations per unit volume to be $(10^6)^{3/2} \text{ cm}^{-3}$, we find for $R_{\Pi} \approx 10^{-4} \text{ cm}$ that $\alpha_{p,\Pi}/\alpha_{p,e} = 0.2\text{--}0.4$ at 15 MHz, which agrees with the experimental results reported in Refs. 112 and 115. This piezofluctuational mechanism explains the basic experimental facts specific to highly inhomogeneous piezosemiconductors, namely, the effective attenuation of sound only for longitudinal waves propagating along a piezoactive direction, the photosensitivity of the sound attenuation coefficient, and the failure of the usual mechanism of attenuation of sound due to the piezoelectric field. When the piezofluctuational interaction is adopted, the large real part of the permittivity of the corresponding CdS and CdSe samples is due to the fact that the original electric field applied along the piezoactive direction gives rise to volume strain and, correspondingly, to an additional electrical displacement which is seen experimentally as an increase in permittivity.

2.2.2. In highly-doped semiconductors, there is little overlap between electron states belonging to different impurities. In accordance with Ref. 74, the dividing line between strong and weak doping in the case of weak compensation is determined by the impurity concentration \bar{N}_i for which we have nonzero conductivity at absolute zero. For example, the Mott metal-dielectric transition in n-Ge occurs for $\bar{N}_i = 1.5 \cdot 10^{17} \text{ cm}^{-3}$. The temperature dependence of the sound attenuation coefficient in the region of this boundary for weak compensation in germanium is shown in Fig. 8 (Ref. 79). The effect of dopant concentration on the sound

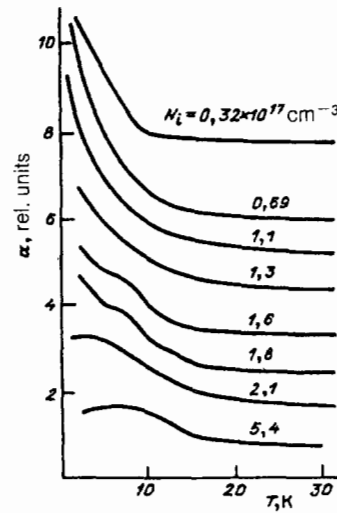


FIG. 8. Sound attenuation coefficient of doped germanium as a function of temperature.

attenuation coefficient, calculated from the data in Ref. 79 for this range of disorder concentrations shows that its contribution falls almost linearly with increasing disorder so long as $N_i < \bar{N}_i$. For $N_i \lesssim \bar{N}_i$, the function $\alpha(N_i)$ is essentially nonlinear and becomes flatter in the region of metal-type conductivity.

It is clear from general considerations that for weak doping and weak compensation, both charge carriers in the band and carriers localized on individual elements of disorder contribute to sound attenuation. Depending on temperature, either contribution can become dominant.

The sound attenuation coefficient due to charge carriers in the band can be calculated from (32) and depends on the specific energy structure of the conduction band.

The contribution of localized charge carriers is discussed in Ref. 122 where it is shown that it is given by

$$\alpha_{\text{loc},e} = \frac{2N_A c_{\text{neut}} (\chi_{\text{loc}}^e)^2 \omega^2 \tau_{\text{loc}}}{9\rho_s^3 k_B T \bar{V} [\exp(4\Delta/k_B T) + 3](1 + \omega^2 \tau_{\text{loc}}^2)}, \quad (53)$$

where c_{neut} is the concentration of neutral carriers of disorder, 4Δ is the orbit-valley energy splitting, and χ_{loc}^e is the deformation potential for localized carriers. For example, for n-type germanium, the orbit-valley interaction ensures that localized electrons can be either in the singlet A_1 or triplet T_2 states, where the separation between these states depends on the type of impurity. Thus, in the case of Sb doping, $4\Delta_{\text{Sb}} = 0.32 \text{ meV}$ whereas for As doping $4\Delta_{\text{As}} = 4.23 \text{ meV}$. The magnitude of the energy splitting determines the temperature range in which the contribution of localized carriers is significant. The electron-phonon deformation potential is not very sensitive to the type of impurity and is equal to 12.4, 13.2, and 13.7 eV for Sb, P, and As, respectively.

If we follow Refs. 79–81, we find that the combination of these two mechanisms can explain the available experimental data. For example, consider the attenuation of sound in n-Ge. We note, first, that analysis of experimental results

gives $\alpha \sim \omega^2$, i.e., the condition $\omega\tau_e \ll 1$ is satisfied in all the experiments reported in Refs. 79–81, 122, and 123.

As the temperature increases, the contribution of localized carriers decreases for $T > 100$ K because there is a reduction both in their concentration and in the relaxation time τ_e which is determined in this temperature range by the scattering of carriers by phonons. Their contribution cannot, probably, be isolated for $T > 100$ K.

Conversely, the rise in α for $T < 15$ K can be related to the contribution of localized carriers because, at these temperatures, the carriers begin to condense on donors and this, on the one hand, leads to an increase in their concentration n_{loc} and, on the other, to an increase in τ_e which is determined in this temperature range by scattering by charged donors and is proportional to N_i^{-1} .

The concentration of disorder produced by the donor dopant was explained in Ref. 79 by assuming that the donor energy level was modulated by the large-scale potential, i.e., the energy gap Δ was so modulated. As N_i increases, the density of states near an energy level is described by a narrower Gaussian, which leads to an increase in the argument of the exponential in the denominator in (53). As far as the first factor in (53) is concerned, most donors are filled because the degree of compensation is small. Unlocalized electrons are scattered by neutral and ionized donors for which $\tau_e \sim N_i^{-1}$, so that $n\tau_e \approx \text{const}$. However, the above approach gives the fact that a rapid increase in the sound attenuation coefficient begins at a temperature at which there is a rapid rise in electrical resistance of semiconductors such as germanium, which is due to hopping conductivity. Moreover as we have already noted, near the Mott transition, where features such as E_2 conductivity have been seen, the sound attenuation coefficient is also found to exhibit certain peculiarities (see Fig. 8). Let us therefore examine another mechanism for the interaction of elastic waves that involves a manifestation of local disorder in weakly doped semiconductors.

The point is that when the degree of compensation is low, many properties of the weakly-doped semiconductors can be explained in terms of charged and neutral complexes that appear in them at low temperatures.⁷⁴ According to these ideas, there are three types of complexes at low temperatures and for low degree of compensation in weakly-doped semiconductors, namely, to so called 0-complexes consisting of acceptors of the same type, which have trapped one electron and are therefore negatively charged, 1-complexes consisting of bound acceptor and ionized donor, so that they are neutral, and 2-complexes consisting of two charged donors and one acceptor between them, so that they are positively charged. Considerations of electric neutrality suggest that the concentration $c^{(0)}$ of the 0-complexes, should be equal to the concentration $c^{(2)}$ of 2-complexes. The binding energy of the complexes is of the order of $q_e^2/\epsilon N_i^{-1/3}$.

A propagating elastic wave alters the separation between the impurities and, consequently, the interaction energy. Since $N_{don} \neq N_{ac}$, $E_{don} \neq E_{ac}$ (N_{don} , N_{ac} , E_{don} , E_{ac} are the donor and acceptor concentrations and ionization energies, respectively), the changes in the concentrations of the complexes are different, and this upsets local electrical neutrality. The concentrations of the 0-complexes and 2-complexes become equal as a result of the redistribution localized carriers. If the displacements of the electrons are looked

upon as random walks, the time τ_{02} for equilibrium to be established is $\sim N_{don,ac}^{-2/3}/D_e$ and we obtain the standard relaxation process in which the relaxation parameter is $\delta N^{(2)} - \delta N^{(0)}$ and $N_{don,ac}$ is the total concentration of disorder. If we now calculate the relaxation sound attenuation coefficient from (8), we obtain

$$\alpha_{02,e} = \frac{c^{(2)} q_e^4 N_A}{\epsilon^2 N_{don}^{-2/3} M s^3 k_B T} \frac{\omega^2 \tau_{02}}{1 + \omega^2 \tau_{02}^2}. \quad (54)$$

If $\alpha \sim \omega^2$, i.e., $\omega\tau_{02} \ll 1$, the transition to impurity conductivity, which is accompanied by a sharp reduction in carrier mobility and, correspondingly, an increase in τ_{02} , gives rise to an increase in α by a few orders of magnitude. For $N_{don} = 10^{16} \text{ cm}^{-3}$, $N^{(2)} = 10^{14} \text{ cm}^{-3}$, $\tau_{02} = 10^{-10} \text{ s}$, and frequency of 500 MHz, we have $\alpha \approx 10 \text{ dB/cm}$, whereas at higher temperatures (about 20 K) and for $\tau_{02} \approx 10^{-12} \text{ s}$, this contribution may compete with the modulation effect of localized transitions.¹²² The features on the temperature dependence of mobilities near the metal-dielectric Mott transition appear in (54) through changes in τ_{02} .

In the case of strong compensation (to be specific we consider an n-type semiconductor), the concentration of electrons originating in the dopant is much lower than the donor concentration. This is why, even at relatively low temperatures, the electron concentration n_e in the conduction band is controlled by thermal band-band transitions. The concentration determines the amplitude of the large-scale potential and the typical size of fluctuations [see (46)].

For $N_{don,ac} \approx 10^{15} \text{ cm}^{-3}$ and $n_e \approx 10^{15} \text{ cm}^{-3}$, $\langle V \rangle$ exceeds $k_B T$ for $T = 100 \text{ K}$ by roughly an order of magnitude and, despite the high concentration of electrons in the conduction band, their spatial distribution is inhomogeneous. Here again we can introduce the concept of the percolation level, so that the attenuation of sound by unlocalized charge carriers can be considered by analogy with highly-doped semiconductors.

However, at low temperatures we have a specific situation because the Fermi level lies below the impurity level and donor pairs are produced with a "shoulder" $r_B \ll r_\omega \ll N_{don}^{-1/3}$ on which there is only one electron. This electron executes transitions between donors which, in accordance with the hypothesis put forward in Ref. 124, is a source of high-frequency electrical conductivity because the electric field upsets the detailed balance of electron transition probabilities between the donors.

If the elastic wave is accompanied by an electric field, we have a process that leads to the attenuation of sound similar to the above dielectric ultrasonic relaxation:

$$\alpha_{pair} = (K_{EE}^2/\epsilon s) \sigma_{xx}(\omega), \quad (55)$$

where $\sigma_{xx}(\omega)$ is the longitudinal high-frequency conductivity. This sound attenuation mechanism was discovered experimentally in the piezosemiconductor CdS in Ref. 125 at gigahertz frequencies at low temperatures, and was subsequently examined in detail in Refs. 126 and 127. It was found in these experiments that although the dc conductivity was exceedingly low so that $\omega\tau_M \gg 1$, the samples had strong photosensitive attenuation of sound that was a function of the intensity and spectral composition of the illuminating

radiation. The first suggestion that the process was due to photoelectrons trapped by shallow impurity centers was made in Ref. 126 where a calculation of ultrasound attenuation by homogeneous piezoelectric crystals was also made, taking into account mobile and localized carriers. The authors of Ref. 126 considered that localization produced additional polarization of the volume because a trapped electron has an 'intrinsic' dipole moment. However, estimates made in Ref. 127 showed that, because of the symmetry of the wave function of the localized electron, the contribution of the polarization effect was lower by roughly three orders of magnitude than the observed result. Moreover, it was established in Ref. 127 that $\alpha \sim \omega^t$ (Fig. 9) where $t \approx 0.9$, which is not in agreement with the Debye frequency dependence that follows from Ref. 126. Moreover, the authors of Ref. 127 found experimentally at the same frequencies that there was a photodielectric effect, and established a proportionality between α and the real part of the permittivity for the different conductivities produced by illumination (see Fig. 9).

These experimental facts were used in Ref. 127 as a basis for a description of losses in terms of the pair hopping model proposed in Ref. 124 for the interpretation of microwave conductivity whereby electrons tunnel from one localization center to another vacant center without activation to the conduction band. If we repeat the discussion given in connection with electrical conductivity, we find that the most relevant are donor pairs with a trapped electron, or without a trapped electron, for which $\omega\tau_{\text{tun},e} \approx 1$ where $\tau_{\text{tun},e}$ is the characteristic tunneling time. This time depends on the separation between the donors and on the height of the potential barrier that must be traversed by the electron. Since in the absence of the wave the transitions occur by the absorption and emission of a thermal phonon, the height of an actual barrier must be $V_{\text{bar}} \sim k_B T$. The dependence of $\tau_{\text{tun},e}$ on distance is exponential for the so-called symmetric pairs, i.e., pairs for which the difference Δ_{pair} between the energies of isolated donor states is zero. This dependence is determined by the exponential dependence of the overlap integral on distance. In general, the barrier height and the overlap integral $I(r)$ are related by

$$V_{\text{bar}}^2 = \Delta_{\text{pair}}^2 + I^2(r). \quad (56)$$

If we combine this with $V_{\text{bar}} \approx k_B T$, we obtain the distribution of $\tau_{\text{tun},e}$, around $\tau_{\text{tun},e}^{(\omega)}$ that corresponds to $\omega\tau_{\text{tun},e}^{(\omega)} \approx 1$.

As a result, the Debye frequency dependence averaged over a broad $\tau_{\text{tun},e}$ distribution is of the power type. Moreover, as explained in Ref. 128, a change in N_{ac} at constant degree of compensation near unity, reduces the frequency dependence of α_{pair} . Thus, for $N_{\text{ac}} \approx 10^{20} \text{ cm}^{-3}$ we have $\Delta\alpha_{\text{pair}} \sim \omega^{0.8}$, and $\Delta\alpha_{\text{pair}} \sim \omega^{0.65}$ for $N_{\text{ac}} = 10^{21} \text{ cm}^{-3}$ ($\Delta\alpha_{\text{pair}}$ is the change in the sound attenuation coefficient of the illuminated sample relative to the dark sample). The difference $\Delta\alpha_{\text{pair}}$ is a very slowly varying function of temperature between 2 and 20 K. An expression for α_{pair} was obtained in Ref. 127 from the pair hopping theory,¹²⁸ taking into account the dependence of the photosensitivity of sound attenuation due to the piezoelectric field on longitudinal conductivity. This yielded a qualitative explanation of the experimental results in which the degree of compensation was treated as an adjustable parameter.

A systematic calculation of the pair-hopping contributions to sound attenuation in terms of the model given in Refs. 124 and 129 was reported in Ref. 130 where the susceptibility of the electron system was determined for arbitrary $\omega\tau_{\text{tun},e}$ for piezoelectric and deformational electron-phonon interactions. In contrast to the piezoelectric interaction, the efficiency of the deformational interaction is determined by the difference between the interaction energies for donors located at x_1 and x_2 :

$$d_{\text{def}} = (\Lambda_{ik}^c u_{ik})_{x_1} - (\Lambda_{ik}^c u_{ik})_{x_2}. \quad (57)$$

For a crystalline semiconductor in which we can ignore the effect of the large-scale potential (46) on the deformation potential, $\Lambda_{ik}^c = \text{const}$ (we know of no estimates of this influence), and $d_{\text{def}} \neq 0$, we must have $(u_{ik})_{x_1} \neq (u_{ik})_{x_2}$. This condition is relatively poorly satisfied up to the gigahertz range. Actually, for $f_s = 5 \text{ GHz}$, the wavelength of sound is about 10^{-4} cm . At the same time, when the concentration of the donor impurity is 10^{15} cm^{-3} , the mean separation between donors is 10^{-5} cm , so that $r_\omega \ll 10^{-4} \text{ cm}$. The lower concentration of donor disorder at constant compensation reduces the attenuation of sound because of the reduction in the number of actual pairs although, of course, it produces an increase in the deformation phase shift between x_1 and x_2 . Explicit expressions for α_{pair} were obtained in Ref. 130 for different types of interaction and different frequencies. If the interaction proceeds via the piezopotential, then in order-of-magnitude estimates we have to put

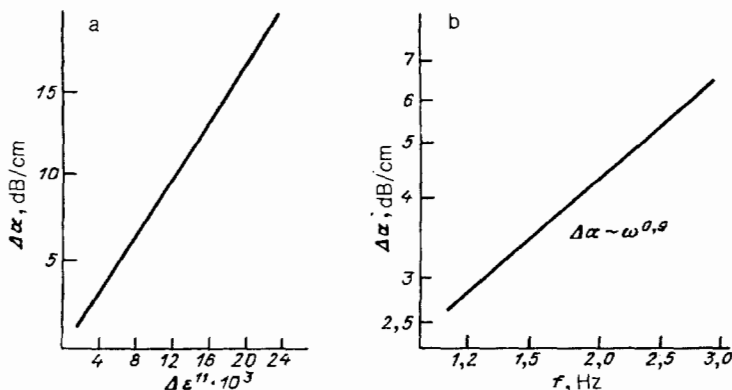


FIG. 9. Photosensitive attenuation of sound as a function of $\text{Im } \epsilon = \epsilon''$ (a) and frequency (b) in compensated CdS.

$$K_{EE}^2 = \beta^2 / \epsilon \rho s^2, \quad (58)$$

in (54), whereas for the deformational interaction we must set

$$K_{EE}^2 = d_{\text{def}}^2 \omega^2 \epsilon / q_e^2 \rho s^4. \quad (59)$$

There are good reasons to expect that the effect will be observed in weakly-doped amorphous semiconductors for which disorder in the host medium can ensure that $(\Lambda_{ik}^e)_{x_1} \neq (\Lambda_{ik}^e)_{x_2}$ although we know of no experimental studies of the deformational interaction of this type. We note in passing that a deformational attenuation mechanism analogous to that considered above for weakly-compensated weakly-doped semiconductors is possible in compensated weakly-doped crystalline semiconductors. The point is that in highly-compensated weakly-doped semiconductors there are in addition to the $N_{\text{don}} - N_{\text{ac}}$ donor pairs with small donor separation and a localized electron, a further N_{ac} negatively charged acceptors and $2N_{\text{ac}} - N_{\text{don}}$ positively charged donors. In the course of deformation produced by the elastic wave, only the energy of the donor pairs changes significantly due to the overlap integral, so that their number must also change. However, this upsets the charge neutrality and gives rise to the diffusion of electrons between nearest acceptors, donors, and pairs, which establishes equilibrium.

The characteristic relaxation time for this process is long because several hops are required over several donors. An approximate formula can readily be obtained from (54) and can then be averaged over the distribution of distances in the donor pairs.

If the sample is not sufficiently well compensated, it is experimentally very difficult to separate the contributions of hopping and band mechanisms in the sound attenuation coefficient. Low temperature studies involving a magnetic field offer this possibility because an external magnetic field distorts the wave function of an electron on a donor with the result that the overlap integral depends on the angle between the dipole moment of the pair and the external magnetic field. Practically all reported studies involving a magnetic field in ultrasonic measurements were performed on p- and n-type InSb with different compensation. The results obtained are discussed in detail in a recent review.¹²¹

2.3. Manifestations of disorder in crystalline conductors

In metallic conductors, local disorder in the form of point defects does not produce such varied manifestations as in semiconductors. It is clear that the reasons for this must be sought in their band structure and the high concentration of free electrons. The result is that, in the entire ultrasonic range, the screening effect of electrons ensures that all the defects can be looked upon as electrically neutral, whatever their intrinsic electronic structure. They therefore affect only the vibrational spectrum of the original lattice, and the presence of free electrons influences only the interatomic forces. Moreover, the high concentration of electrons ensures, because of screening in the long-wave case, that their motion is only slightly perturbed by electromagnetic fields created by deformation in the ultrasonic wave. The attenuation of sound associated with the modulation of the electron distribution function by the elastic wave via the deformation potential,¹³¹ and also with the high concentration of

carriers, is found to be small, and the corresponding sound attenuation coefficient is determined by the electron mean free path which at moderate temperatures in typical crystals is short in comparison with the wavelength of sound up to the gigahertz range (because of collisions between electrons). For the same reasons, the mean free path is practically independent of temperature and of disorder concentration at temperatures of the order of 100 K.

The modulation of the phonon distribution function by the phonon deformation potential can in principle lead to effects similar to those discussed above for dielectrics. In the case of longitudinal waves, they are very difficult to demonstrate experimentally even in high-grade metals because of processes associated with thermal conduction in which the leading part is played by electrons (and not phonons) which ensure relaxation times that are short in comparison with the phonon relaxation times. The sound attenuation coefficient associated with electronic thermal conduction increases in proportion to the temperature together with the thermal conductivity.¹³²

Numerical estimates of the sound attenuation coefficient above the Debye temperature¹³³ yield

$$\alpha_{\text{met}} \sim (T/T_D)(\omega/\omega_D)^2.$$

As in the case of dielectrics, a temperature gradient is not established for shear waves propagating in highly-symmetric directions, so that, in principle, it is possible to investigate the contribution of local disorder to collective phonon processes. However this is very difficult to do experimentally because the growth process in metallic crystals is accompanied by the appearance of a large number of dislocations as compared with dielectrics. The dislocational contribution thus becomes comparable with, and often greater than, the contribution of phonon processes. Since the concentration of dislocations and the length of dislocation loops can be measured directly only on the surface of metallic crystals, the interpretation of experimental ultrasonic data must be conducted with considerable caution despite the large number of publications on dislocation effects in ultrasonic measurements (see, for example, Ref. 78). This is due to the fact that the frequency and temperature dependence of α is very sensitive to the combined effect of ultrasonic frequency and dislocation parameters such as the length of dislocations and of the individual oscillating segments, the mechanism responsible for the damping of the oscillations of dislocations, and so on. The introduction of local disorder changes the length of the dislocation segments oscillating in the ultrasonic wave and, hence, the entire contribution of dislocations to the attenuation of sound. This is why in each specific experimental situation we have to analyze the combined frequency, temperature, concentration, and (whenever possible) amplitude dependence of α before we can separate the contributions of the different mechanisms. The wider are the variations, the more reliable will be the conclusions that can be drawn in this way. The most convenient approach is to investigate the interaction between dislocations and non-thermal disorder when the latter is produced by illumination. These questions are examined in detail in the review given in Ref. 134. The principal conclusion there, from our point of view, is that the contribution of dislocations that interact with disorder decreases with increasing tempera-

ture. This means that high-temperature acoustic measurements are an effective means of separating out the manifestations of local disorder.

All that we have said so far is also valid for the experimental detection of the direct interaction between elastic waves and thermal and nonthermal local disorder. In the latter case, studies of the orientational dependence of α in different waves are particularly effective. It is precisely for this reason that the redistribution of elastic dipoles produced by nonthermal local disorder has been investigated in particular detail in metallic crystals. At temperatures up to 600–700 K, the low mobility of elastic dipoles ensures that the frequency at which acoustic measurements are made is usually less than 1 MHz (see, for example, Ref. 22). The measurement range is extended in Refs. 18 and 135 to 1200 K and up to 100 MHz. Metals with the bcc structure have been investigated in particular detail (they include W, Mo, V, Nb and Fe + 3% Si). High frequencies were used to excite different types of wave (longitudinal, fast and slow shear) in small crystals in different directions^{100,110,111} (Fig. 10). Analysis of the orientational dependence of α obtained for a given crystal can be used to determine the components of the tensor Ω_{ik} and thus obtain information about the distortions due to local disorder of a particular type in the lattice.¹³⁵ Moreover, as already noted, analysis of the position of the maximum of α on the temperature scale at different frequencies can be used to estimate the height of the barrier involved in the reorientation of the carrier of local disorder. For example, a niobium single crystal was used in Ref. 18 in experiments with longitudinal waves in the [110] direction, and it was found that the barrier height was approximately 33 kcal/mole, whereas for shear waves propagating in the same direction the corresponding figure was about 26.4 kcal/mole. This order of magnitude of activation energy corresponds to displacement of oxygen atoms within the unit cell. The difference between the activation energies can be ascribed to the fact that the deformations produced in these waves gave rise to displacements in different crystal directions and therefore involved tunneling through different potential barriers.

The reduction in the contribution of dislocations with increasing temperature enables us to use the high-temperature range for studies of thermal disorder, especially since the concentration of the latter rises exponentially with in-

creasing temperature. Measurements in metals with the bcc structure are particularly suitable for these purposes in the case of longitudinal waves propagating along the space diagonal for which nonthermal disorder in the form of elastic dipoles is found to be ineffective.¹⁸ Such measurements of the sound attenuation coefficient have been made on Al, W, Mo, V (Ref. 18), Ni (Ref. 135), In, Sn, and Pb (Ref. 136). Figure 11 shows the results obtained for Al with longitudinal waves propagating in the [111] direction at 15, 25, and 55 MHz. The experimental procedure was such that only the change in the sound attenuation coefficient, $\Delta\alpha(T)$, was measured as a function of temperature. The temperature range was 300–800 K and the measurements showed that $\Delta\alpha(T)$ had a maximum whose position shifted toward higher temperatures with increasing frequency, as predicted by the theory. The rise in $\Delta\alpha$ continues at higher temperatures. Since the melting point of aluminum is 903 K, it was possible to establish the conditions under which local disorder in the form of Frenkel' defects can become significant. If we use (24) to analyze the experimental data in Ref. 18, we find that $V_2 = 0.55$ eV, $v_1 = 0.9$ eV, $\tau^* = 3 \times 10^{-13}$ s, which means that the energy of formation of a Frenkel' defect in the form of a vacancy plus and interstitial atom is about 0.7 eV. This value is in good agreement with the defect formation energy calculated from entropy measurements reported in Ref. 63. Inclusion of the interaction between the elastic wave and thermal disorder, and also the dislocation contribution (dashed curve in Fig. 11) results in reasonable agreement between calculations and theory.

A monotonic rise in $\Delta\alpha$ without a frequency dependence has been observed in high melting-point metals at all frequencies in the range 15–85 MHz, suggesting that the condition $\omega\tau_{c,i} \gg 1$ was satisfied. It is then possible [see (21)–(28)] to calculate the height of the barrier that must be overcome in the creation of local disorder. The barrier height is found to be 0.3, 0.29 and 0.27 eV for tungsten, molybdenum and niobium, respectively. These figures are very close to the values of $k_B T_m$ (0.32, 0.25, 0.24 eV, respectively) and this was used in Ref. 18 to conclude that the carriers of local disorder in high-melting-point metals for $T < T_m$ are crowdions, the creation of which produces 'local melting,' i.e., the shifting of the linear chain of atoms from the positions of equilibrium. Similar results were also observed in nickel at the same frequencies, but the measure-

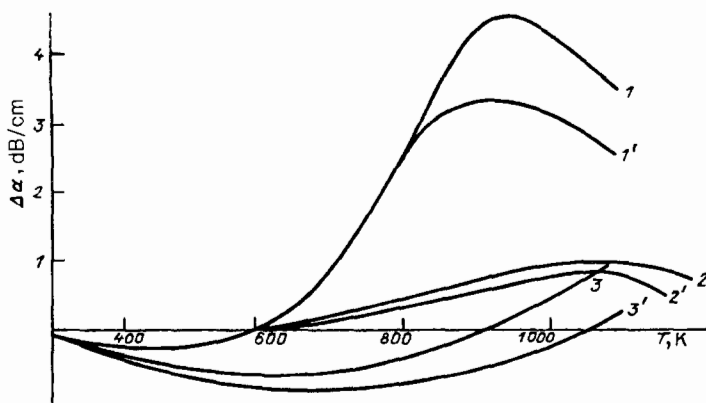


FIG. 10. Sound attenuation coefficient in niobium; 1, 1'—fast shear wave, 2, 2'—slow shear wave, 3, 3'—longitudinal wave, 1–3—25 MHz, 1'–3'—15 MHz.

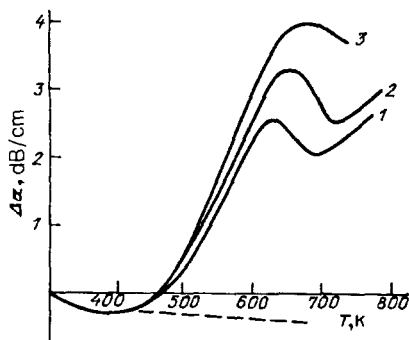


FIG. 11. The sound attenuation coefficient for longitudinal waves in aluminum as a function of frequency for the following frequencies: 15 MHz (1), 25 MHz (2), and 55 MHz (3).

ments were performed in a saturating magnetic field in order to exclude the contribution of magnetic processes to $\Delta\alpha(T)$.

The measurements were performed in Ref. 136 at lower frequencies (up to 10 MHz) at temperatures in the range 400–500 K, using longitudinal and shear waves in different crystallographic directions. Some metals were found to exhibit a maximum of $\alpha(T)$ whereas others were found to have monotonically strongly increasing $\alpha(t)$. Analysis of experimental results based on (21)–(23), using independent measurements of creation and annihilation energies of Frenkel' defects obtained from positron annihilation experiments,¹³⁷ gave good agreement with experiment. We note by the way that it was found in Ref. 137 that these low-melting-point metals had an anomalously low concentration of thermal point defects, which was reflected in the low values of the attenuation coefficient determined by the resonance method. This is probably also related to the linear variation of the elastic moduli of these metals with increasing temperature, which extends right up to the melting point.

We note in passing that the determination of the contribution of local disorder from the temperature dependence of elastic moduli requires considerable caution if the condition $\omega\tau_{c,t} \approx 1$ is not satisfied, since it is essential to exclude a variety of factors such as temperature effects in the energy of interatomic interaction due to changes in anharmonism, including thermal expansion, changes in the nature of bonds in semimetals and semiconductors, and so on. An analysis of different situations in a number of dielectrics, semimetals, and semiconductors was reported in Ref. 23. In the following Section we confine our attention to the effect of topological disorder on the numerical values and temperature dependence of elastic moduli.

2.4. Manifestations of disorder in superionic conductors

Superionic conductors are materials with ionic conductivity whose numerical value exceeds $0.1\Omega^{-1}\text{cm}^{-1}$ and whose activation energy is low (about 0.1 eV). It is therefore difficult to draw a sharp boundary between ionic crystals and superionic conductors on the basis of their electrical properties because, as will be seen from the references given below, acoustic effects that are in some way related to ionic conduction are often due to superionicity.

Nevertheless, structurally, there is no doubt about the properties of ionic conductors, i.e., we can speak of a specific superionic phase in which the number of spatial potential energy minima for one of the ionic components significantly exceeds the number of ions of this component. The result is a sharp rise in the mobility of one of the ionic components as compared with ordinary ionic crystals whereas other components form a stable crystal lattice. We thus have a particular form of disorder where in the interior of the periodic structure produced by ions of a particular type there are more mobile ions of another type, whose concentration, mobility, and interaction with the stationary lattice may vary between different crystals within relatively wide limits. For example, in β -AgI, which exists below 400 K, we know¹³⁹ that the iodine ions form a hexagonal lattice and the silver ions lie in the interior of regular tetrahedrons.

The transition to the α -phase occurs above 420 K. In this phase, the iodine ions form a bcc lattice and, in the silver sublattice, there are 42 almost equivalent crystallographic positions for every 2 cations [12 equivalent tetrahedral positions, i.e., 12 (d), 24 positions with coordination number equal to 3, i.e., 24 (h), and, six octahedral positions, i.e., 6(b)]. The largest volume for the silver ions lies in the interior of distorted tetrahedrons in the 12 (d)-positions and the smallest volume lies in the interior of the distorted octahedrons in the 6 (b)-positions. The transition from the β -phase to the α -phase is accompanied by a jump in the electrical conductivity by four orders of magnitude and a reduction in the activation energy by a factor of several times.

In another typical superionic conductor, namely, α - RbAg_4I_5 , 16 ions of silver are distributed over 56 interstices.¹⁴⁰ These 56 interstices consists of two sets of 24 equivalent positions (Ag II and Ag III) and 8 equivalent positions (Ag-c). The Ag II positions form pairs arranged so that they cannot be simultaneously occupied by silver ions. At temperatures above 208 K, the Ag II positions (transition to the α phase) contain a substantial number of mobile ions and play an important part in the geometry of conducting channels typical for superionic structures.

The close correlation between the behavior of acoustic parameters and translational ionic mobility can be illustrated by the example of PbF_2 . This is a superionic conductor which also has a high electrical conductivity at high temperatures, which is mostly due to Frenkel' defects and interstitial anions.¹³⁸

Neutron scattering data obtained for PbF_2 show that, at the upper limit of the specific heat anomaly ($T \approx 625$ K), about 30% of the fluorine atoms leave the (1/4, 1/4, 1/4) sites. The process then continues at a slower rate up to the melting point (Fig. 12a). Figure 12b shows the temperature dependence of the sound attenuation coefficient and other elastic moduli¹⁴¹ from which it is clear that the increasing α and the significant change in the elastic moduli occur precisely in the temperature range in which ions transfer to new positions in the lattice, the predominant one being (1/3, 1/3, 1/3). These positions lie at the center of the face of the tetrahedron consisting of lead ions¹³⁸ and, probably, are characterized by a significantly shallower energy minimum as compared with a lattice site. It is interesting to note that the transition to the superionic state is accompanied by a significant change in the elastic moduli due to the volume change in the wave. On the other hand, the elastic modulus c_{44} is

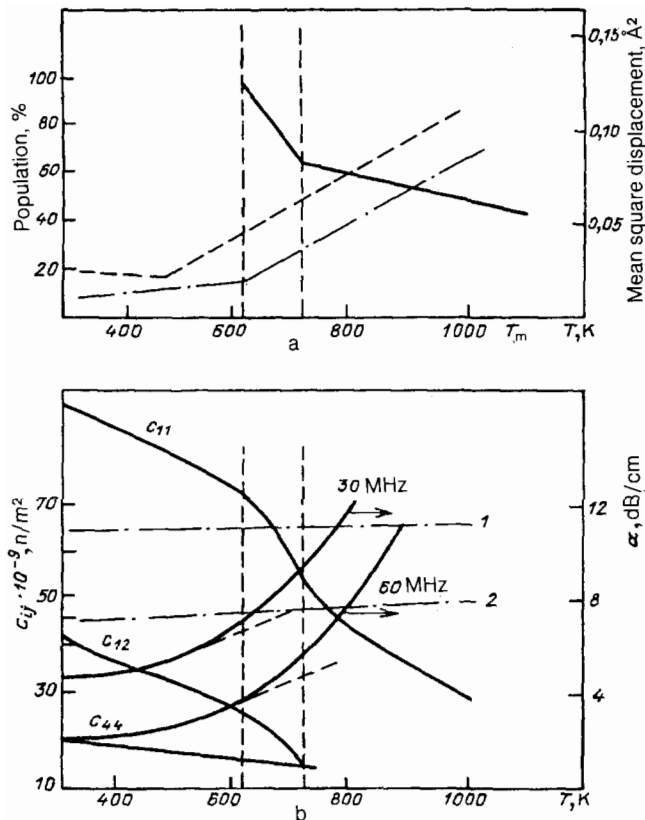


FIG. 12. The change in the crystal parameters of PbF_2 accompanying the transition to the superionic state. Dashed curves—calculated values¹⁴¹ for 25% and 50% occupation of the sites (curves 1 and 2, respectively).

unaffected by the appearance of the mobile ions. The contribution to the elastic moduli of PbF_2 due to the change in the occupation of interstices was calculated in Ref. 141 using the theory reported in Ref. 142 for 25% filling (dot-dash curve 1 in Fig. 12b) and 50% filling (dot-dash curve 2 in Fig. 12b). The change in the filling of the interstices can be used to explain the behavior of elastic moduli during the onset of superionic conductivity, but their temperature dependence is found to be very different.

The loss of stability in part of the lattice and the appearance of disorder in the system of anions or cations leads to a $\sim 30\%$ change in the modulus c_{12} . The contribution of Frenkel' defects is discussed phenomenologically in Ref. 143 and is calculated in Ref. 141, but the experimental results could not be explained.

The close correlation between the dc behavior of $\alpha(T)$ and $\sigma(T)$ has also been noted for typical superionic conductors such as $\alpha\text{-RbAg}_4\text{I}_5$ (Refs. 144 and 145) and also $\beta\text{-AgI}$ (Ref. 146) and so on.

All this shows that the dominant mechanism of the interaction between elastic waves and the ionic subsystem is the interaction with carriers responsible for the dc conductivity which, judging by the sound attenuation coefficient, are almost delocalized charge carriers in the semiconductors. Analysis of conductivity measurements¹⁴⁷ shows that the concentrations of localized and delocalized charge carriers produced by the damaged sublattice in superionic conductors are very similar. For example,¹⁴⁷ in $\alpha\text{-AgI}$ at 427 K, the concentration of delocalized ions is about 25%; at 630 K,

the figure is 60%. In RbAg_4I_5 at 230 K, the concentration of mobile ions is 2.5% and the figure at 300 K is 10%. Moreover, in accordance with the estimates reported in Ref. 147, the subdivision of mobile ions into localized and delocalized is generally somewhat arbitrary.

Thus, at the above temperatures, the time spent by a mobile ion localized and delocalized states in $\alpha\text{-AgI}$ is 0.9/1.4 ns and 0.6/0.9 ps, respectively, whereas for RbAg_4I_5 the figures are 0.15–6 ps and 0.25–2.5 ps.

If the ionic conductor exhibits the piezoelectric effect then, as in piezosemiconductors, the source of the imposed force that leads to the redistribution of mobile carriers is the piezoelectric field accompanying the elastic wave. Precisely the same situation obtains in dielectrics with appreciable ionic conductivity: $\beta\text{-AgI}$ (Ref. 146), Ag_3SbS_3 (Ref. 148), $\text{Ag}_8\text{HgS}_2\text{I}_6$ (Ref. 149), LiIO_3 (Refs. 150–152), and $\text{Li}_2\text{B}_4\text{O}_7$ (Refs. 152 and 153). The dc conductivity of these materials lies in the range $0.1\text{--}0.001 \Omega^{-1} \text{ m}^{-1}$ which enables us to observe the relaxation maxima of $\alpha(T)$, with σ being regulated by the temperature, in the megahertz frequency range.

The sound attenuation coefficient is as before described by (37), and the difference between the character of motion of mobile ions and free electrons in semiconductors can be taken into account by means of the frequency function $\sigma(\omega)$ by analogy with inhomogeneous semiconductors. The electrical conductivity of superionic conductors has been determined in a variety of different lattice and continuum models,^{138,147} and also by using the two-well potential with one well of the order of $k_B T$ (Ref. 144).

The physical difference between these models is that, in the former, the function of the external electric field is to produce only the drift of the mobile charge carriers (that occupy the shallow potential wells), whereas in two-well potentials, the external electric field modifies the transition probability between the potential minima and then produces the directed drift of excess carriers that have entered the shallow well. The result of all this is a shift of the 'center of gravity' of the explanation of the origin of the Drude-type frequency dependence of $\sigma(\omega)$, well known from numerous experiments. For example, in continuum models, the motion of ions is regarded as continuous in the highly anharmonic periodic potential of the skeleton. Restoring forces acting at the minima of the potential produce oscillatory motion which is replaced by diffusion once the barriers are overcome. The mobility $\mu_i(\omega)$ can be calculated in terms of the ion velocity correlator written as a continued fraction.¹⁵⁴ In the simplest case of a two-term continued fraction, we have

$$\mu_i(\omega) = \frac{e_1 q_i / m_i}{e_1^2 + e_2^2 \omega^2} + \frac{i \omega e_2 q_i / m_i}{e_1^2 + e_2^2 \omega^2},$$

$$e_1 = r_i - \frac{\tau_U \langle U''(x) \rangle / m_i}{1 + \omega^2 \tau_U^2}, \quad e_2 = 1 - \frac{\tau_U^2 \langle U''(x) \rangle / m_i}{1 + \omega^2 \tau_U^2}, \quad (60)$$

where m_i is the mass of the mobile ion (carrier), r_i is the 'coefficient of friction' representing the interaction between the mobile ion and the oscillations of the skeleton ions (ions of the unmelted lattice), $\langle U''(x) \rangle$ is the second space derivative of the ion energy in the potential well of the skeleton, averaged over the volume, and τ_U is a measure of the time spent by the ion at the minimum of U . Substituting (60) in (37), we obtain

$$\alpha_{si} = \frac{K_{EE}^2}{2s} \frac{(N_i q_i^2 e_1 / \epsilon m_i) / (e_1^2 + e_2^2 \omega^2)}{\left(1 + \frac{N_i q_i e_2 / \epsilon m_i}{e_1^2 + e_2^2 \omega^2}\right)^2 + \left(\frac{N_i q_i e_1 / \omega \epsilon m_i}{e_1^2 + e_2^2 \omega^2}\right)^2}. \quad (61)$$

In the case of the piezoelectric field accompanying the elastic wave, we have, as before,

$$K_{EE}^2 = \beta^2 / 2\epsilon \rho s^2.$$

When $e_2 \omega \ll e_1$

$$\mu_i(\omega) = \mu_i(0) = q_i m_i^{-1} / e_1, \quad (62)$$

and (61) becomes identical with the Gurevich–White formula with a Maxwellian relaxation time since $\sigma_i = q_i \mu_i N_i$. The approximate form of (61), given by (62), describes the contribution of ionic conduction to the attenuation of sound in piezoelectric crystals.

In some complex crystals that exhibit the piezoelectric effect and ionic conduction,¹⁴⁸ the measured positions of the maxima of α are found to be different from the positions corresponding to Maxwellian relaxation inhomogeneous materials for $\mu_i(\omega) = \mu(0)$. This demonstrates either that μ_i is frequency dependent or there are local electric fields that are associated with fluctuations in the concentration of ions, similarly to what happens in the inhomogeneous semiconductors discussed above.

We note in passing that it is relatively easy to detect experimentally the attenuation of sound by the Gurevich–White mechanism because it is anisotropic and is seen only in the case of piezoactive waves. If there is no piezoelectric effect, the interaction between the elastic wave and the mobile ions is of the deformational type. The sound attenuation coefficient for this case is estimated in Ref. 144 as the ratio of the Joule heat per unit volume to the energy of the elastic wave. Dimensional considerations apparently lead to the expression

$$\alpha'_{si} = (\sigma(0) / \epsilon s) (\omega r_{2w,i} / s)^2, \quad (63)$$

where $r_{2w,i}$ is the separation between the shallow minimum of the two-well potential and the saddle point.

Mobile ions can contribute to the attenuation of sound via the deformation potential in the same way as in semiconductors. However, the elastic wave now modulates the depth of the potential wells in conducting channels and not the edges of the conduction band. This causes a redistribution of mobile ions over the wells, i.e., an electric current, since the number of wells is much greater than the number of mobile ions. The electromechanical coupling coefficient can be calculated from (59) in which q_i must be interpreted as the ion charge.

Since the deformational interaction is characterized by a very strong frequency dependence of the sound attenuation coefficient, the experimentally determined relation $\alpha \sim \omega^2$ in such typical superionic crystals as RbAg_4I_5 (Ref. 145) and PbF_2 (Ref. 141) can be explained by assuming that $\mu_i(\omega) \sim \mu_i(0) / \omega^2$ ($e_2 \omega > e_1$) at frequencies of a few dozen MHz because we know that $\sigma(\omega)$ of superionic conductors is described by the Drude formula and $\omega \tau_M \gg 1$ (typically, the magnitude of $\sigma(0)$ in superionic conductors is about 100

$\Omega^{-1} \text{ m}^{-1}$). The result of all this is that we obtain not only a quadratic frequency dependence of α , but also $\alpha \sim \sigma(\omega)$, in agreement with experiment. The order-of-magnitude estimate for α is 0.2–0.8 dB/cm, which is also in agreement with experimental data.

The attenuation of sound may also be due to charge carriers localized in the two-well potential. They are the analogs of donor pairs with one localized electron, and are responsible for sound attenuation in semiconductors. However, since in the case of superionic and ionic conductors we are interested in temperatures of 100 K or above, we have over-barrier carrier transitions. Moreover, in contrast to semiconductors, two-well potentials can be assigned particular positions in the lattice, which means that each well in a pair has its own deformation potential, say, Λ_1 and Λ_2 , respectively. Moreover, the ‘shoulder’ of the pair, r_{pair} , is a constant, so that, even if we take $r_{\text{pair}} \ll \lambda$ into account, the transitions of an ion in a pair are due to the difference $\Lambda_1 - \Lambda_2$ and not to the deformation gradient. The result is that the ultrasonic wave modulates the transition probabilities between the potential wells (as in the above ultrasonic relaxation), and this produces a change in the polarization. The corresponding sound attenuation coefficient in the absence of the piezoelectric effect is [cf. (54) and (59)]

$$\alpha_{\text{loc},i} = \frac{(\Lambda_1 - \Lambda_2)^2 N_{\text{pair}}}{2k_B T \rho s^3} \frac{\omega^2 \tau_{\text{loc},i}}{1 + \omega^2 \tau_{\text{loc},i}^2}, \quad (64)$$

where N_{pair} is the number of symmetric singly-filled potential wells (symmetric wells are defined as those for which the pre-exponential factor in the expression for the relaxation time, $\tau_{\text{loc},i}$, is the same on the right and on the left of the saddle point; $\tau_{\text{loc},i} = \tau_{\text{loc},i}^* \exp(V_{\text{loc}} / k_B T)$ where V_{loc} is the barrier height that must be overcome in a transition from one well to the other in the pair). Similarly to the case of semiconductors, the expression given by (63) can be readily generalized to the superionic semiconductor exhibiting a piezoelectric effect.

It is clear that, when the times of dielectric (on localized ions) and Maxwellian relaxations on mobile ions are very different, the two mechanisms operate independently. In the opposite case, the two mechanisms must be considered together, using the standard set of equations in which the permittivity has both real and imaginary parts:¹⁵⁴

$$\begin{aligned} \epsilon &= \epsilon_1 - i\epsilon_2, \\ \epsilon_1 &= \epsilon_0 + \frac{\Delta\epsilon}{1 + \omega^2 \tau_{\text{loc},i}^2}, \\ \epsilon_2 &= \epsilon_0 + \frac{\Delta\epsilon \omega \tau_{\text{loc},i}}{1 + \omega^2 \tau_{\text{loc},i}^2}, \end{aligned} \quad (65)$$

where ϵ_0 is the permittivity of the unmelted lattice and $\Delta\epsilon$ is the relaxation part of the permittivity. It is readily shown that for the deformational interaction

$$\Delta\epsilon = q_i r_{\text{pair}} (\Lambda_1 - \Lambda_2) / k_B T.$$

The experimental separation of piezoelectric and deformational mechanisms must as before rely on the orientational relations. Moreover, the application of a steady external electric field E_0 that has a different effect on the two

components (through translational mobility and the change in the pair population) may be useful.

Another approach to the evaluation of the sound attenuation coefficient in superionic conductors is proposed in Ref. 154. To ensure that one type of ions is fixed, it is assigned a mass of 1 000 times the mass of the mobile ions. The transport coefficients that appear in the sound attenuation coefficient and are associated with viscosity (shear and bulk) and thermal conduction (volume expansion coefficient and thermal conductivity) are calculated from the experimental radial distribution function $g(r)$ for different temperatures and a suitably chosen pair potential. This yields a quadratic frequency dependence for α and the required order of magnitude for RbAg_4I_5 , Ag_3Si , and PbF_2 . Of course, the total neglect of the periodic potential can hardly be justified, but calculations performed in the spirit of the liquid model can be used to isolate the contribution of the unmelted lattice. Experiment shows that the sound attenuation coefficients of melts of superionic conductors (salts; see Ref. 156, for example) are not very different, indicating that the effect of the periodic potential is quite small. Other theoretical models that have been used with varying degrees of success to calculate the sound attenuation coefficient of superionic conductors are described in Refs. 157 and 158.

In addition, we also note the recent investigation reported in Ref. 160 in which a study was made of the superionic (proton) conductors CsDSO_4 and CsHSO_4 . The transition to the superionic state in these materials is very well defined: the elastic moduli are reduced by 50% and the sound attenuation coefficient increases by an order of magnitude. In the superionic state, the investigated temperature interval is small and it is difficult to draw any conclusion about the temperature dependence of α . Nevertheless, it is concluded in Ref. 160 that the attenuation of sound is due to the redistribution of local disorder within the unit cell of the main crystal lattice. However, because electrical conductivity data are not reproduced, it is quite difficult to draw any conclusion about the dominant relaxation mechanism.

The main experimental results and computational schemes employed for superionic conductors and ionic conductors thus show that the sound attenuation coefficient can contain contributions due to nonlocalized and localized manifestations of disorder in one of the ionic subsystems. The main criterion for distinguishing between the mechanisms that manifest themselves in the course of nonlocalized motion is $\alpha \sim \sigma(\omega)$ and $\alpha \sim \omega^2$. The mechanisms responsible for electrical conduction and sound attenuation are identical. Hence acoustic experiments, which are more difficult than electrical experiments, are also more promising in the case of low-resistivity superionic conductors as a means of excluding the effect of electrical contacts on experimental data, and also when different types of wave are employed. This can be used to determine the components of the deformation tensor from data on $\sigma(\omega)$ and $\sigma(0)$.

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