

Disorder and order in long-wave high-temperature acoustics (II): monatomic liquids

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(Submitted 27 April 1992)

Usp. Fiz. Nauk **162**, 111–181 (November 1992)

Manifestations of order in topologically disordered media are analyzed. Amorphous materials and monatomic melts are considered as examples of disordered media. It is shown that in the case of close-packed liquids geometric and chemical short-range order are most clearly manifested in the acoustic properties. In these materials ordering is of a dynamical character. The temperature dependence of the acoustic properties correlates well with the results of x-ray and neutron diffraction methods of investigation and substantially supplements the latter. The contributions from loss of long-range order and intensification of thermal translational motion on melting are distinguished from one another by comparing the bulk moduli of elasticity of melts, crystals, and amorphous substances.

1. ACOUSTIC EFFECTS IN MEDIA WITH TOPOLOGICAL DISORDER

Many (but by no means all) manifestations of local order in media with crystalline long-range order were considered in Ref. 1. The direct interaction of low-frequency sound with lattice atoms or ions at quite high temperatures was described in terms of relaxation theory, in which explicit expressions for the sound absorption coefficient and sound speed dispersion were found by calculating the thermodynamic functions within the weak-solution model. In this model the periodically arranged atoms (ions) undergoing harmonic oscillations comprised the solvent and the atoms (ions) participating in the translational motion played the role of the solute. Experimental and theoretical studies of these processes, as a rule, make it possible to identify the relaxational mechanism and, on this basis, to determine the structural units participating in the translational motion and their concentration and the heights of the potential barriers to translational motion as well as (see below) to reconstruct the components of the strain tensor of the crystal lattice due to carriers of local disorder.

It is completely obvious that a substantially different approach is needed in order to study the acoustic properties of noncrystalline materials. First of all, crystalline order cannot play the role of the zero-order approximation (solvent). Second, the concentration of disorder is high and the weak-solution theory becomes meaningless. Third, the type of disorder must be specified in order to choose an appropriate model.

In this paper we consider media with topological disorder—amorphous materials and melts of chemically comparatively simple substances.

Before discussing the results of long-wave acoustic experiments and their theoretical interpretation, we make some general remarks concerning the characteristic features, which could be manifested in the acoustic properties, of the structure and thermal motion in amorphous bodies and melts.

All condensed media with topological disorder exhibit common macroscopic uniformity and short-range order, manifested in the existence of preferred values of nearest-neighbor distances and coordination numbers. Significant

differences can be easily seen, however, by comparing for an amorphous material and a melt the radial distribution functions determined from diffraction experiments on the one hand and computed within the hard-sphere model on the other.

It is well known (see, for example, Ref. 2 and the bibliography provided there) that the hard-sphere model, which takes into account only geometric order due to the impenetrability of the walls of the spheres, describes quite well the behavior of $g(r)$ for many metallic melts (liquid semimetals and semiconductors require special analysis). However, the functions $g(r)$ for amorphous films exhibit significant differences (see, for example, Refs. 3 and 4). Comparing $g(r)$ for an amorphous film to $g(r)$ for, as an example, molten iron⁵ showed that although the position of the first peaks is virtually the same in both materials, the first peak in the case of the amorphous film is significantly sharper and the second peak exhibits fine structure, i.e., it splits into two peaks of different height. In addition, in the amorphous film oscillations of the $g(r)$ are observed up to appreciably larger values of r than in the molten iron.

At the present time there is no unequivocal interpretation of the fine structure of the peaks in $g(r)$ in amorphous materials. But, the existence of the peaks itself indicates that there are present in the structure regions with nongeometric order. This result is the physical basis for the interpretation of experiments on sound absorption, which indicate unequivocally the existence of a relaxation mechanism of sound absorption at both low and high temperatures.

The point is that in the absence of special types of interactions of elastic waves with matter (for example, the piezoelectric effect and ferromagnetism) the only source of sound absorption are deformational and thermoelastic interactions. Numerical estimates and analysis of the temperature dependences of the Akhiezer sound absorption coefficient, made with the help of formulas derived for imperfect crystals (see the bibliography and formulas in Ref. 1), show that most existing experimental results on $\alpha(\omega)$ and $\alpha(T)$ in different amorphous materials require a different interpretation. Diffusion of structural units and heat fluxes due to gradients of deformation in a wave (see the formulas from Ref. 1) are also found to be ineffective right up to frequencies of

10^9 Hz (thin films are an exception). For this reason, without specifying the relaxation mechanism, we can assert that sound absorption requires the existence of regions whose deformational potentials differ from either one another or the environment. It is only then that an elastic wave creates an effective potential relief which changes the probability for structural units of the amorphous material to overcome natural potential barriers (the change in the probability of transitions through a barrier is determined by the gradient of the deformation interaction constant¹).

The most significant difference between amorphous and melted substances is associated with their shear modulus G . In the case of amorphous substances G can be considered to be frequency independent at all temperatures below the softening temperature T_g , whereas in the case of melted substances the shear modulus in nonviscous (viscosity $\eta' \leq 10^3$ kg/m·sec) melts is virtually zero at all frequencies of the applied force right up to the relaxation frequencies of shear viscosity, which are equal to $\sim 10^{12}$ Hz. According to the general ideas of Ya. I. Frenkel', this indicates that in amorphous bodies and melts two different types of thermal motion of the atoms are realized, in spite of the similarity of the instantaneous structures of these materials. In the first case most atoms (ions) occupy quite deep (compared with the thermal energy) potential wells and they undergo primarily oscillatory motions around disordered positions of equilibrium. Only a small fraction of the structural units is capable of participating in translational motion. From this standpoint, topological disorder in amorphous bodies can be termed static. In the second case, i.e., in melts, all atoms (ions) participate in the translational motion and they also probably execute oscillatory motions at the same time.

Since for low-viscosity metallic and semiconductor melts the characteristic relaxation times of the shear viscosity τ_η are $\sim 10^{12}$ sec, a large number of spatial configurations of the atoms is realized during the period of the sound wave or during the propagation of the wave through the sample. It is natural to term such topological disorder as dynamical disorder.

Thus in the sequence crystal—amorphous state—melt the first two states, in which the short-range character of the thermal motion is preserved, have substantially different order characteristics (according to the third definition of V. Dal'; see the first reference in Ref. 1 of this article). This makes it possible, by comparing the sound speeds (elastic moduli) and sound absorption coefficients of substances with the same chemical composition but in different states (crystalline and amorphous), to observe different manifestations of static topological disorder in both the acoustic and other properties.

Great care must be taken, however, in interpreting the results of such a comparison, since the interpretation is not always unique. There are several reasons for this. First, the amorphous state is a thermodynamically nonequilibrium state, and for this reason all structure-sensitive properties, in particular, the acoustical properties, depend on the thermal history of the sample. For this reason, temperatures far from the softening point are preferable for determining the effect of order on, for example, the speed of elastic waves. In addition, it is probably useful to perform measurements in a range of temperatures in order to make sure that there is no temperature hysteresis in the sound speed. However, since

the speeds of longitudinal and shear waves depend on the structure of an amorphous material, these measurements can be used to check the parameters of the real structure of the material. Second, the effect of order on the elastic moduli is masked by relaxation processes, which can be manifested differently in the crystalline and amorphous states. In the presence of a relaxational process (see, for example, Ref. 1) the sound speeds contain a frequency-dependent correction Δs . In order to calculate this correction it is necessary to know the specific scheme of the relaxational process. Since $\Delta s \sim (1 + \omega^2 \tau^2)^{-1}$, the highest possible frequencies and comparatively low temperatures (increasing τ) are best for revealing the effect of order.

In addition, it is useful to measure s and α simultaneously, since irrespective of the relaxational mechanism (see Ref. 1)

$$\Delta s/s = \alpha s / \omega^2 \tau, \quad (1)$$

and, therefore, τ can be estimated from Eq. (1), if Δs and α are determined experimentally (the notation is explained in Ref. 1).

The effect of the character of the thermal motion on both relaxational processes and the elastic moduli can be determined experimentally by comparing the acoustical characteristics of amorphous materials and melts and in the process the applicability of different models of the liquid state can be assessed. As in the case of amorphous materials, great care must be exercised in separating the contributions of the changed character of the thermal motion and relaxation, even though, as is well known, the liquid state is a thermodynamically equilibrium state. This is connected with the short relaxation times characteristic for liquids. Thus, if $\tau \approx 10^{12}$ sec and the typical values are used for α , i.e., $\alpha \approx 10^{-1}$ cm⁻¹ at 100 MHz, then $\Delta s/s \approx 0.2$, which can mask the change in the sound speed on melting of the crystal.

1.1. Amorphous materials

It is well known⁶ that the amorphous state, irrespective of the manner in which it is produced, is, in contradistinction to melts, a thermodynamically nonequilibrium state, and as a result of these different characteristics, including, and sometimes especially, the acoustical characteristics, have long relaxation times. Moreover, measurement of elastic-wave speeds, which are uniquely related to the elastic moduli of the structure, is often an effective method for observing aging, results of heat treatment, etc. For this reason, in comparing the properties of amorphous materials it is best to employ data for samples having approximately the same age, thermal history, and so on, assuming that the elastic moduli found under such conditions are the equilibrium moduli of the structure existing at a given moment. Such precautions are apparently not necessary for studying most glassy dielectrics, which age much more slowly than glassy metals. The higher stability of glassy dielectrics is manifested also in the fact that they are easily obtained in the form of bulk samples, while metallic and semiconductor structures can be produced only in the form of films, thin ribbons, etc.

Strongly pronounced hysteresis phenomena are observed in the temperature dependences of the acoustical characteristic of metallic glasses with increasing and decreasing temperature, even at temperatures appreciably below the crystallization point. The magnitude of hysteresis

depends on the maximum temperature to which the sample is heated. Definite uniqueness can be achieved by first subjecting the sample to temperature normalization in the form of annealing at a definite (with respect to the crystallization point) temperature and for a definite period of time. In this situation, low-temperature measurements of the elastic moduli as a function of the annealing temperature may be very informative. As an example, Fig. 1 displays such a dependence, taken from Ref. 7, for the alloy $\text{Fe}_{83}\text{B}_{17}\text{P}_{10}$.

As far as the physical reasons for these effects are concerned, the increase of the elastic moduli with increasing temperature is apparently associated primarily with the outflow of excess free volume, for example, by recombination of Frenkel' pairs.⁵ This reduces the degree to which the amorphous phase departs from an equilibrium state and makes more likely the formation of crystal-like clusters. As shown in Ref. 8, at low temperatures there is virtually no outflow of free volume. Thus, for alloys with high cobalt concentration the effective outflow of free volume starts only at temperatures of 500–550 K.

Another reason is associated with the possibility of formation of a cluster structure in the amorphous alloy. For example, the dependence of the sound speed on the annealing temperature in Fig. 1 is explained⁷ with the help of the so-called model of a cluster in a shell. In this model it is assumed that because of the rigidly oriented bonds the specific cluster—cluster interface energy is appreciably higher than the cluster—metallic solid solution interface energy. For this reason, an interlayer of solid solution can remain between the clusters. The entire temperature dependence of Young's modulus can be explained by the change in cluster size as a function of the annealing temperature.⁷ There also exist more complicated models, employed for qualitative interpretation of acoustic experimental data,^{6,9–12} but these models also suffer from inadequate substantiation. Nonetheless, there is no doubt that the degree to which the structure of metals and elementary semiconductors in the amorphous state departs from equilibrium, which, as a rule, decreases with increasing annealing temperature and time, is responsible for the acoustical hysteresis in these materials.

The above-noted phenomena, together with possible manifestations of fast relaxation processes, make it much more difficult to separate the contribution of static topological disorder to the acoustical properties of a material.

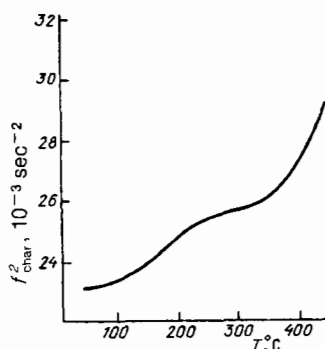


FIG. 1. Characteristic frequency of the sample as a function of the annealing temperature.

Another problem arising in any attempt to separate this contribution is the choice of suitable acoustic properties, since a crystal is an anisotropic structure and the speeds and absorption coefficients of elastic waves in it are functions of the direction of propagation, while in glass and melt all properties are isotropic. The most suitable characteristics are, apparently, the bulk modulus K and the shear modulus G , which in the case of a crystal can be calculated in terms of the elastic moduli for different types of lattices^{13,14} while in the case of glass they can be calculated in terms of the speed s_l of longitudinal waves and the speed s_t of shear waves:

$$\rho s_l^2 = K + (4G/3), \quad \rho s_t^2 = G.$$

Even such a comparison entails, however, some arbitrariness, since, although K , defined as the relative change in volume under hydrostatic compression, remains meaningful for crystals, polycrystals, and amorphous substances, the numerical value of the shear modulus depends on the direction of application of the force with respect to the slip plane of the crystal. The room-temperature bulk and shear moduli K_{cr} and G_{cr} are presented in Table I for a number of crystals with cubic symmetry, together with the same moduli K_{pcr} and G_{pcr} for polycrystals of the same metals.^{10,16} It is obvious that the latter crystals, which do not have static topological disorder, are isotropic due to the random distribution of the orientation of the crystallites. Data for amorphous materials are also presented here. According to Table I, in metals the transition from the crystal to the polycrystal and the amorphous state is not accompanied by significant changes in the bulk modulus (up to 10%) and shear modulus (30–40%). For example, in the case of a transition from the crystalline state into an amorphous state the bulk modulus changes by 6.2% for $\text{Pd}_{80}\text{Si}_{20}$, 6.5% for $\text{Pd}_{77.5}\text{Cu}_{6.5}\text{Si}_{16.5}$, and 4.5% for $\text{Sm}_2\text{Co}_{12}$.¹⁵ In other words, the metallic bond is insensitive to both changes in the long-range order (intercrystallite boundaries) and even loss of long-range order.

In elemental semiconductors and dielectrics, in which interatomic interaction is realized by means of covalent bonds, the transition into an amorphous state results in a significant reduction of both the bulk and shear moduli. Thus, the bulk and shear moduli of crystalline germanium and silicon calculated from the elastic moduli¹⁷ using the formulas of Ref. 14 were found to be $K_{\text{cr}} = 7.1 \cdot 10^{10}$ Pa and $G_{\text{cr}} = 4.7 \cdot 10^{10}$ Pa for Ge and $K_{\text{cr}} = 9.2 \cdot 10^{10}$ Pa and $G_{\text{cr}} = 5.8 \cdot 10^{10}$ Pa for Si (at 293 K). At the same time, the values of $K + (4G/3)$ calculated from the data on longitudinal sound speeds in amorphous Ge and Si were found to be $4.8 \cdot 10^{10}$ and $4.5 \cdot 10^{10}$ Pa, respectively.¹⁸

Similar results for the change in the bulk and shear moduli with the transition into the glassy state are also obtained for chalcogenide semiconductors and quartz glasses.

Therefore, because they are directed toward the nearest neighbors, covalent bonds are more sensitive to loss of long-range order than are metallic bonds, since for semiconductors, dielectrics, and metals the volume changes at a transition into the amorphous state are virtually identical. The small change in the bulk moduli in amorphous metals (several percent) indicates that the free volume arising in the amorphous state (several percent) is distributed uniformly between separate structural units. Conversely, such a strong change in the bulk moduli in amorphous semiconductors

TABLE I. Comparison of volume and shear elastic moduli of crystals (cr), polycrystals (pcr), and amorphous materials (AM).

Element	$K_{cr} \cdot 10^{-10}, \text{Pa}$	$G_{cr} \cdot 10^{-10}, \text{Pa}$	$K_{pcr} \cdot 10^{-10}, \text{Pa}^{1)}$	$G_{pcr} \cdot 10^{-10}, \text{Pa}^{1)}$	$K_{AM} \cdot 10^{-10}, \text{Pa}$	$G_{AM} \cdot 10^{-10}, \text{Pa}$
Al	7,64 [146]	2,61 [146]	7,25 [16]	2,64 [16]	—	—
Cu	13,71 [146]	4,73 [146]	13,60 [16]	4,55 [16]	—	—
Cd	5,35 [146]	2,42 [146]	4,07 [16]	1,94 [16]	—	—
Zn	6,83 [146]	3,94 [146]	6,85 [16]	4,06 [16]	—	—
Ni	18,75 [146]	9,29 [146]	17,61 [16]	7,7 [16]	—	—
Fe	17,31 [146]	8,69 [146]	15,98 [69]	8,21 [69]	—	—
Fe ₈₀ B ₂₀	—	8,8 [15]	—	—	14,1 [15]	6,5 [15]
Fe ₆₀ Ni ₂₀ B ₂₀	—	—	—	—	20,6 [15]	6,1 [15]
Fe ₄₀ Ni ₄₀ B ₂₀	—	—	—	—	16,7 [15]	6,0 [15]
Pd	19,23 [146]	4,74 [146]	—	—	—	—
Pd ₈₀ Si ₂₀	19,3 [15]	4,69 [15]	—	—	18,2 [15]	3,5 [15]
SiO ₂	5,65 [146]	4,24 [146]	—	—	3,7 [20]	3,1 [20]
Si	9,78 [146]	6,65 [146]	—	3,43 [69]	2,5/2,9 ²⁾	1,8/1,4 ²⁾
Ge	7,54 [146]	5,48 [146]	—	—	2,45/3,0 ²⁾	1,8/1,4 ²⁾

¹⁾The densities are taken from Ref. 69.

²⁾Calculated from the values of the limiting speed of sound¹⁸ for Poisson ratios 0.2/0.3.

and dielectrics can be interpreted as a nonuniform distribution of free volume, giving rise, in terms of percolation theory, to weak key couplings between clusters with large (of the order of crystalline) values of the elastic moduli.

This interpretation from investigation of the equilibrium elastic moduli agrees with a numerical experiment performed on a 500-atom model of an amorphous material.¹⁹ In this model three atoms were removed from the central part so as to form a vacancy cluster. If the model relaxed under the action of the Lennard-Jones potential, then with time only 10% of the initial volume of the vacancy cluster remained and the remaining volume was distributed uniformly over the system. If, however, covalent bonds were introduced between the atoms, then the vacancy cluster did not vanish, i.e., the presence of a covalent bond was sufficient to stabilize the local free volume.

For the reasons mentioned above, the temperature dependence of the elastic moduli of metallic glasses is uninformative from the standpoint of the investigation of physical processes, while the temperature dependence of the speeds of longitudinal and shear waves have been studied in detail in a wide range of temperatures in amorphous dielectrics and semiconductors (Ref. 20; see bibliography there). These temperatures dependences were found to be extremely diverse. Thus, in amorphous SiO₂, GeO₂, and BeF₂ the temperature coefficients of the sound speed (TCS) were found to be positive, i.e., the sound speed increases on heating. Conversely, in chalcogenide glasses TCS was negative and increased with increasing selenium concentration.

Since the TCS of the corresponding single crystals is negative and as a rule large, a decrease or change in sign of the TCS in amorphous materials requires special study. One reason could be the presence of one or several relaxation processes in the amorphous material. Indeed, irrespective of the specific relaxation mechanism, its contribution to the sound speed is always negative and proportional to $(1 + \omega^2\tau^2)^{-1}$.¹ For many relaxational processes the coefficient of proportionality decreases with increasing temperature as T^{-1} . For this reason, if $\omega\tau \ll 1$, then due to relaxation the TCS will decrease or can change sign. For example, it has been established for SiO₂ that at frequencies up to 16 GHz

maxima of the relaxational type are observed in the sound absorption coefficient as a function of the temperature. In addition, in the lower megahertz range $\alpha \sim \omega^2$, and the coefficient of proportionality is $\approx 10^{-17} \text{ dB} \cdot \text{sec}^2/\text{cm}$.²⁰ Setting $\tau = 10^{-11} \text{ sec}$ and using the formula (1), we obtain for Δs as an estimate of several tenths of s , which gives for TCS the correct order of magnitude and sign. Moreover, since $\Delta s \sim T^{-1}$, the relaxational contribution to the sound speed decreases with increasing temperature, and this could give rise to the change in sign of the resulting TCS, i.e., a transition from TCS > 0 to TCS < 0, as is observed experimentally.

Positive values of TCS could also be due to elastic micrononuniformity of glasses, as proposed in Ref. 20 and associated, for example, with structural nonuniformities. In this model the bulk and shear moduli are given by

$$K = K' - (\bar{\Delta}_K^2)^{1/2}, \quad G = G' - (\bar{\Delta}_G^2)^{1/2}, \quad (2)$$

where K' and G' are the values of the moduli in a uniform material and $\bar{\Delta}_K^2$ and $\bar{\Delta}_G^2$ are the squares of the corresponding spatial fluctuations. If the temperature coefficients of K' and $\bar{\Delta}_K^2$ or G' and $\bar{\Delta}_G^2$ are different, then it can be expected that TCSs will also be different. This is why fluctuations of the glass density are ineffective for this approach. However, the application of the model to glassy dielectrics (which was first proposed in order to explain the TCS of these materials) is questionable, since there is no hysteresis in the temperature dependences of the sound speed in them, and therefore within the model the elastic nonuniformities vanish with increasing temperature and then on cooling reappear in exactly the same form as before heating. Indirect arguments also indicate that positive values of the TCS are associated with relaxational processes. In Table II the Poisson ratios ν are calculated for different glassy dielectrics and semiconductors from the speeds of longitudinal shear waves given in Ref. 20:

$$\nu = \frac{1}{2} \frac{s_l^2 - 2s_t^2}{s_l^2 - s_t^2}.$$

Table II also gives data on the TCS for these glasses for s_l and s_t .

TABLE II. Poisson's ratio for some amorphous substances.

Substance	ν	$\text{TCS} \cdot 10^6, \text{K}^{-1} (s_l)$	$\text{TCS} \cdot 10^6, \text{K}^{-1} (s_l)$
SiO ₂	0,17	+130	+110
GeO ₂	0,19	+70	+5
BcF ₂	-0,72	+200±50	+100±50
As ₂ S ₃	0,25	-150	-170
As ₂ Se ₃	0,25	-170	-150
Se	0,31	-640	-1000

According to Table II, glasses with positive values of the TCS have small and even negative Poisson ratios. In accordance with the formula for ν , this is a consequence of the fact that s_l is less than s_t . In isotropic media, nonisotropic (with respect to deformation) relaxational processes are unlikely to arise, i.e., as observed experimentally, relaxational processes are manifested more effectively in longitudinal waves. As a result, s_l decreases due to the relaxational correction with s_t remaining constant and ν decreases.

Sound absorption has been investigated in a large number of amorphous materials in a wide range of frequencies and temperatures. This includes metallic glasses, elemental amorphous semiconductors Si, Ge, and Se, chalcogenide semiconductors, glassy dielectrics, and other materials. The results of low-temperature experiments have been interpreted quite convincingly on the basis of two-level tunneling systems (TLTS) (see bibliography in Ref. 21). Measurements of the sound speed and sound absorption coefficient at quite high temperatures (~ 100 K and higher) have not been analyzed as carefully.

Relaxational maxima have been observed in measurements of $\alpha(T)$ in metallic glasses. It is by no means always possible to establish unequivocally the nature of these maxima. This has been done most convincingly in the case of the relaxation of dissolved hydrogen as well as in the case of Gorskiĭ relaxation.^{4,22}

When crystalline metals are hydrogenated their lattice expands by approximately 3 \AA^3 per H atom, even though the H atoms occupy interstices. In the process there arises an elastic dipole, which is manifested in ultrasonic measurements.

Approximately the same change in volume is obtained for metallic glasses simultaneously with observation of relaxation. This is usually attributed to the appearance of elastic dipoles also in the glasses. Direct measurements of the structure by the x-ray method in Nb₃Ge have shown that the peak of the radial distribution function splits into two subpeaks, the splitting being associated with the presence in the matrix of pairs of atoms whose separation is increased due to the presence of H.¹⁵ The peak in α associated with hydrogen relaxation is asymmetric: It is flatter on the low-frequency side and its width is three to four times greater than the Debye width. The activation energy ΔE and the preexponential factor τ_0 are found by measuring the displacement of the peak in α as a function of the temperature and finding the location of the peak on the frequency scale. The results of different studies agree quite well with one another. Thus, according to the measurements in Ref. 15 in the alloy Pd₈₀Si₂₀ $\tau_0 \approx 5 \cdot 10^{-13}$ sec and $\Delta E = 0.31$ eV, while according to Ref. 22 $\tau_0 = 1.4 \cdot 10^{-14}$ sec and $\Delta E = 0.34$ eV. The

energy in the exponential of the relaxation time is close to the activation energy of self-diffusion of hydrogen in the alloy, determined from independent measurements to be 0.25 eV. The agreement is improved, if the spread in the heights of the potential barriers to diffusional motion is taken into account in the spirit of percolation theory. As a result of this spread, the effective barrier in the exponential of the diffusion coefficient drops below the average value.²⁴ This decrease is determined by the variance of the barrier heights. The barrier reduction is ~ 0.08 eV for a uniform distribution and 0.06 eV for a normal distribution.

The observation of so-called Gorskiĭ relaxation—diffusion of impurities and characteristic defects in the material from regions of compression into regions of tension—at frequencies of hundreds of kilohertz and even megahertz is associated not with the physical features of amorphous materials but rather with the fact that metallic glasses and amorphous semiconductors are obtained primarily in the form of thin films. As a result, in microscopically uniform media the deformation gradients produced by an elastic wave are inversely proportional not to the wavelength λ but rather the film thickness h , since $\lambda > h$ and, hence, the characteristic relaxation time is, in order of magnitude,¹

$$\tau'_D = h^2 / \pi^2 D, \quad (3)$$

and the absorption coefficient is determined by Eq. (25) of Ref. 1.

The characteristic relaxation time determined by heat fluxes changes similarly, i.e., instead of τ_T we have

$$\tau'_T = h^2 \rho C \tilde{\nu} / \pi^2 \kappa, \quad (4)$$

and the relaxation mechanism itself is called Gorskiĭ relaxation.²⁵

Using the typical values of the kinetic coefficients, we find the τ'_D and τ'_T in films tens to hundreds of angstroms thick is 10^{-6} – 10^{-9} sec. For this reason, ultrasonic measurements can be a valuable source of information on the kinetic coefficients of amorphous films.

In the absence of impurities, and also when the frequency range of the measurements excludes gradient mechanisms, the interpretation of the relaxation maxima is closely connected with the possibility of atoms, molecules, or structural units participating in the translational motion under the action of deformation in an elastic wave. As mentioned above, this requires the existence of regions where the deformational potentials are different from the environment, i.e., regions where the interatomic interaction potential is different from that in the environment or the spatial symmetry (degree of order) is different from the mean-statistical sym-

metry over the sample. In what follows, we term such regions defects in a topologically disordered medium.

The concentration of such defects in amorphous materials is low, and this makes it possible to employ once again, for calculating the sound absorption coefficient and the dispersion of the sound speed, just as in crystals, the weak-solution approximation,¹ in which the specific relaxational scheme is determined by the model adopted for the defect and the solvent is the spatially uniform disordered medium with short-range order, for example, the hard-sphere model.

Of course, from a general-physics standpoint, defects in amorphous materials and in crystals have nothing in common. In crystals defects are regions where long-range order is disrupted and as a consequence the entropy of the system increases. In amorphous systems defects are any formations which in some sense are different from the environment and for this reason they decrease the entropy of the system, since they decrease the number of microscopic states corresponding to a given energy of the disordered medium.

We underscore the fact that irrespective of the type of defect a disordered system in the energy representation can be regarded in the simplest case as a two-level system, since the translational motion of some structural unit, as noted above, can be described as one or several transitions of the entire ensemble from one energy state into another.

In the general case defects in amorphous alloys, just as in crystals, can be divided²⁶ into point, extended microscopic, and macroscopic. Defects of the first kind consist of broken and irregular bonds, pairs with variable valence, atoms with a weak stress field (quasivacancies), atoms with a strong stress field (quasiembedded atoms), and small clusters consisting of several atoms and containing the disruptions noted above. Linearly extended defects can consist of the boundaries of clusters, accumulations of quasivacancies, etc.

Investigations with an electron microscope have shown that linear defects are virtually absent in amorphous metallic alloys, in spite of the fact that free volume is undoubtedly present.⁴ Positron-annihilation experiments have not revealed a large number of localized vacancy-like defects.⁴

For this reason, the concept of three types of defects in metallic glasses was developed in Refs. 27 and 28. These defects include three types of clusters containing 15–20 atoms: n-type—characterized by low “internal” hydrostatic pressure; p-type—characterized by high pressure; and, r-type—characterized by high shear stresses. Estimates based on the mechanical properties and from density data give n- and p-defect concentrations of ~2.5%. Defects can migrate through the volume and recombine. Similar ideas were employed in Refs. 29 and 30 to describe diffusion in amorphous metals by means of small displacements of complexes.

Another mechanism of diffusion³¹ in amorphous metallic alloys is also based on the presence of complexes, but the complexes are distinguished not by internal pressure but rather according to the number of metal atoms surrounding the metalloid. According to the model, complexes containing the maximum admissible number of metal atoms are rare, i.e., in terms of percolation theory the concentration of unsaturated complexes is higher than the percolation threshold, and this makes it possible for an atom to move from one complex to another, i.e., it enables diffusion over macroscopic distances. In this approach the defects are com-

plexes in which the number of metal atoms surrounding the metalloid is different from the average number.

Thus the analog of a vacancy is a complex with $n - 1$ atoms and the analog of an interstitial atom is a complex with $n + 1$ atoms.

Modulation of the defect concentration in the sense of deformation in a wave, as considered above, i.e., the concentration of energetically more favorably organized defects increases under the action of the elastic wave, as studied in Ref. 1 for crystals, can provide a quite universal mechanism of interaction of an elastic wave with a topologically disordered medium. The concentration changes due to diffusion of metal atoms either from a defect into the surrounding medium and vice versa (into the matrix), or from the defect into another.

It is obvious that, repeating the same arguments as for point defects in crystalline metals, the interaction energy for an elastic wave interacting with a constituent atom of a defect in a topologically disordered medium can be written as

$$E_{\text{int}}^{(m)} = K_l^{(m)} \Omega_{ik}^{(m)} u_{ik} \equiv \Lambda_{ik}^{(m)} u_{ik}, \quad (5)$$

where $K_l^{(m)}$ is the local bulk modulus in a defect of type m ; the tensor $\Omega_{ik}^{(m)}$ characterizes the difference of the deformation produced by an atom in a defect of type m from that of the matrix; and, $\Lambda_{ik}^{(m)}$ is the deformation potential of a defect of type m . If the wavelength of the wave is much greater than the size of the defects and the distances between defects, then the force inducing diffusion of atoms is the difference of the corresponding components of the deformation potential in different defects. Assuming that the diffusion process consists of uncorrelated jumps, the relaxation times, describing the change in a number of atoms comprising a defect or recombination of defects, can be estimated as r_d^2/D' and r_{bd}^2/D'' , respectively, where r_d is the characteristic of a defect, r_{bd} is the characteristic distance between defects, and D' and D'' are the diffusion coefficients for diffusion over distances r_d and r_{bd} .

If defects are assumed to be noninteracting, then because of their low concentration it can be assumed that $r_d \ll r_{bd}$. Therefore the transition of an atom between defects requires a much larger number of jumps than a transition inside a defect, i.e., D'' is apparently close to its macroscopic value and the relaxation process itself is characterized by a comparatively narrow spectrum of relaxation times.

The transformation of n, p, and r type defects into one another can be taken into account within the theory of chemical relaxation,³² modified in Ref. 33 for analyzing the contribution of complex-formation processes to sound absorption in solids. Since, however, the interpretation of existing experimental facts on sound absorption and sound speed in amorphous materials (see below) does not require this approach, we do not discuss it.

If defects of the types n and p interact with one another, striving to occupy adjacent positions, or a defect is produced by the changing composition of metal atoms around a metalloid or the extreme atoms migrate from the defect into the matrix or vice versa, then in order to migrate from one state (environment) into another an atom must overcome a potential barrier V . Sound absorption in this situation is due to breakdown, as result of deformation in an elastic wave, of thermal equilibrium between transitions through the bar-

rier, i.e., the mechanism of sound absorption is analogous to absorption in crystalline metals due to thermal disorder.

Thus the physical processes responsible for sound absorption in amorphous metals are very similar to those in crystalline metals. The difference stems from the fact that, due to the manifestation of random configurations in the short—and intermediate—range orders of amorphous media, the characteristic sizes of defects and the distances between defects as well as the local values of the bulk moduli, deformation potentials, and potential-barrier heights in the general case are random variables and must be characterized by a distribution function $G(\Lambda, r, V)$.

For this reason, the procedure for calculating, for example, α , reduces to calculating the sound absorption coefficient for a single defect (pair of defects) α_1 and then summing α_1 over all defects weighted by the distribution function $G(\Lambda, r, V)$:

$$\alpha = \int \alpha_1 G(\Lambda, r, V) d\Lambda dr dV, \quad (6)$$

where α_1 is the sound absorption coefficient calculated in Ref. 1 for crystals, per defect.

We consider first relaxational processes associated with recombination of defects of the types n , p , and r , which require, as noted above, overcoming a series of potential barriers. Generally speaking, in order to calculate the sound absorption coefficient it is necessary to calculate the effective height of a potential barrier for displacement over a distance r_{bd} . This is a typical problem in percolation theory.²⁴ However, we assume that the diffusion coefficient D is a known parameter of the problem. This assumption makes unnecessary averaging over V and we can set $\tau_{bd} = r_{bd}^2/D$. As far as averaging over r_{bd} is concerned, if the defects are distributed randomly, then the distribution function of the distances between defects $G_1(r_{bd})$ is

$$G_1(r_{bd}) = 4\pi N_d^2 \exp(-\frac{4}{3}\pi N_d r_{bd}^3), \quad (7)$$

where N_d is the total number of defects.

If the distribution of the distance between defects is statistically independent of the distribution of the deformation potentials, we can write

$$G(r, \Lambda) = G_1(r_{bd}) G_2(\Lambda),$$

where $G_2(\Lambda)$ is the distribution function of the deformation potentials of the defects. Then

$$\alpha_{bd} = \sum_{q,t} \frac{2\pi \bar{\Lambda}_{q,t}^2 N_q N_t}{\rho s^3 k_B T} \int_0^\infty \tau_{bd}^2 \exp\left(-\frac{4}{3}\pi N_d r_{bd}^3\right) \frac{\omega^2 \tau_{bd}}{1 + \omega^2 \tau_{bd}^2} d\tau_{bd}, \quad (8)$$

where $\bar{\Lambda}_{q,t}^2 = \int \Lambda_{q,t}^2 G_2(\Lambda) d\Lambda$ is the standard deviation of the deformation potentials of different defects (the tensor indices in the components of the deformation potential, distinguished by the form of the deformation u_{ik} in the elastic wave, are omitted), N_q and N_t are the number of defects of types q and t (where q and t assume the values n , p , and r), and $\Lambda_{q,t} = \Lambda_q - \Lambda_t$.

It is easy to see that α_{bd} has an absolute maximum as a function of frequency, if

$$\omega = DN_d^{2/3}. \quad (9)$$

In order to estimate the temperature dependences of α_{bd} we replace the exponential in Eq. (7), which truncates $G_1(r_{bd})$ for $r_{bd} > N_d^{-1/3}$, by $1 - H(r_{bd}) - \bar{r}_{bd}$, where $H(r_{bd})$ is the Heaviside unit step function, $\bar{r}_{bd} = \gamma_{bd} N_d^{-1/3}$, and γ_{bd} is a numerical factor of order 1. Then

$$\alpha_{bd} = \sum_{q,t} \frac{2\pi \bar{\Lambda}_{q,t}^2 N_q N_t}{\rho s^3 k_B T} \left[D r_{bd} - \frac{D^{3/2}}{4\sqrt{2}\omega^{1/2}} F_1(\bar{r}_{bd}, D, \omega) \right],$$

where

$$F_{1(2)} = \pm \ln \frac{\bar{r}_{bd}^2 + \sqrt{2} \bar{r}_{bd} (D/\omega)^{1/2} + (D/\omega)}{\bar{r}_{bd}^2 - \sqrt{2} \bar{r}_{bd} (D/\omega)^{1/2} + (D/\omega)} + 2 \arctan \frac{\sqrt{2} \bar{r}_{bd} (D/\omega)^{1/2}}{(D/\omega) - \bar{r}_{bd}^2}. \quad (10)$$

For low and high frequencies the functions $\alpha(\omega)$ are identical to relaxation functions, though the functions themselves are substantially different. In addition, this mechanism is distinguished by the fact that its temperature dependence is closely correlated to the temperature dependence $D(T)$, i.e., $\alpha(T)$ increases with T . Moreover, it can happen that at low temperatures $D/\omega < \bar{r}_{bd}^2$ while at high temperatures the reverse inequality holds. Then the function $\alpha(\omega)$ is replaced by a quadratic law $\alpha \sim \omega^2$.

The dispersion of the sound speed is calculated similarly to Eq. (10):

$$\frac{\Delta s_{bd}}{s} = \sum_{q,t} \frac{2\pi \bar{\Lambda}_{q,t}^2 N_q N_t}{\rho s^3 k_B T} \frac{D^{3/2} \omega^{-3/2}}{4\sqrt{2}} F_2(\bar{r}_{bd}, D, \omega). \quad (11)$$

It can be shown, as done above, with the help of asymptotic expansions that the above-noted properties of α_{bd} as a function of frequency and temperature, as compared with the relaxation behavior, are also manifested in $\Delta s_{bd}/s$.

The quantity α_d , associated with the exchange of atoms between defects and the matrix, can be calculated similarly. This mechanism can be interpreted as the above-mentioned diffusion of free volume. If the process of formation of extended defects is viewed as uncorrelated flow of Z_d excess atoms, which create internal mechanical stresses, into a region of radius r_d , then for $N r_d^3 \gg 1$ the probability of such a process is described by the normal distribution (N is the total number of atoms). Depending on whether $Z_d > 0$ or $Z_d < 0$, we have different defects. For this reason, for purposes of estimation, the probability of the appearance of a defect of type n having radius r_d and containing a smaller number of atoms in the region r_d , is of the order of $\Phi[(N r_d^3)^{1/2}]/2$, and the probability for defects of type p is $[- \Phi((N r_d^3)^{1/2}) + 1]/2$, where $\Phi(k)$ is the error function. Substituting the probability of formation of defects into Eq. (6), we obtain, for example, for defects of type n ,

$$\alpha_d^n = \frac{\bar{\Lambda}^2 N}{4\rho s^3 k_B T (\Delta r_d)} \int_{r_{d1}}^{r_{d2}} \Phi((N r_d^3)^{1/2}) \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} dr_d, \quad (12)$$

where $\Delta r_d = r_{d1} - r_{d2}$, and r_{d1} and r_{d2} are the minimum and maximum sizes of the defects, respectively.

Since the second factor in the integrand has a sharp maximum at $r'_d = (D_d/\omega)^{1/2}$, for purpose of estimation the function $\Phi(x)$ can be removed from the integrand and evaluated at $r_d = r'_d$, and the limits of integration can be extended from 0 to ∞ . Then

$$\alpha_d^n = \frac{\bar{\Lambda}^2 N \Phi([N(D_d/\omega)^{3/2}]^{1/2}) D_d^{1/2} \omega^{1/2}}{4 \rho s^3 k_B T (\Delta r_d)}. \quad (13)$$

It is easiest to estimate the variance of the sound speed if $(Nr_{d1})^{1/2} \gg 1$:

$$\frac{\Delta s_d^n}{s} = - \frac{\bar{\Lambda}^2 N (D_d/\omega)^{1/2}}{\rho s^2 k_B T (\Delta r_d)} (F_1(r_{d2}, D_d, \omega) - (F_1(r_{d1}, D_d, \omega))). \quad (14)$$

Similar expressions can be derived for other types of defects, taking into account the possible difference in the intradefect diffusion coefficients D_d . Since in typical defects $Nr_d^3 \gg 1$, the error function is essentially equal to 1. For this reason, the expression (13) also gives an estimate for the absorption coefficient with a uniform size distribution of defects in the range $r_{d1} < r_d < r_{d2}$.

If relaxation proceeds via single jumps, i.e., by breaking of the bonds of an atom with its nearest neighbors, an over-barrier transition, and establishment of new bonds, the sound absorption coefficient can be calculated using the expression for α (Ref. 1) associated with defects in the manner of Frenkel', together with averaging over the distribution of the heights of potential barriers:

$$\alpha_V = \frac{\bar{\Lambda}^2 N_V}{2 \rho s^3 k_B T} \int_{V_{\min}}^{V_{\max}} G_3(V) \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} dV, \quad (15)$$

where $\tau = \tau_0 \exp(V/k_B T)$, $V > k_B T$, and N_V is the number of atoms participating in a single transition over the random barriers V .

Since the formula (15) has been used repeatedly for interpreting experimental results for both amorphous metals and dielectrics (see below), we list the assumptions on which it is based:

1. The potential barriers V are symmetric.
2. The potential wells differ only in that their deformation potentials are different.
3. The heights of the potential barriers separating two potential wells between which an atom makes a transition and the deformation potentials of each of these wells are independent random variables.
4. There is no direct Coulomb interaction between the potential wells (for amorphous metals this assumption is justified by the high concentration of mobile charge carriers and for dielectrics, probably, by the large distances between the wells).

In order to find explicit expressions for $\alpha(\omega, T)$ and $s(\omega, T)$ it is necessary to calculate the integral in Eq. (15), i.e., to use an explicit expression for $G_3(V)$. Since there are no well-founded physical arguments for choosing the distribution function of the heights of the potential barriers,

$G_3(V)$ is often chosen to be a uniform distribution³⁴ or a Gaussian distribution.^{35,36}

For the uniform distribution we have³⁴

$$\alpha'_V = \frac{\bar{\Lambda}^2 N_V \omega}{2 \rho s^3 \Delta V} [\arctan(\omega \tau_{\max}) - \arctan(\omega \tau_{\min})], \quad (16)$$

where

$$\Delta V = V_{\max} - V_{\min}, \quad \tau_{\max} = \tau_0 \exp \frac{V_{\max}}{k_B T}, \quad \tau_{\min} = \tau_0 \exp \frac{V_{\min}}{k_B T}$$

and V_{\max} and V_{\min} are the maximum and minimum of the admissible heights of the potential barriers. The characteristic experimental manifestations of this mechanism include weak temperature dependence of α and the fact that α is proportional to the frequency ω of the elastic wave.

The sound-speed variance associated with this relaxation process was calculated in Ref. 37:

$$\frac{\Delta s}{s} = \frac{\bar{\Lambda}^2 N_V}{8 \rho s^2 \Delta V} \left(\frac{\Delta V}{k_B T} - \frac{1}{2} \ln \left| \frac{1 + \omega^2 \tau_{\max}^2}{1 + \omega^2 \tau_{\min}^2} \right| \right). \quad (16')$$

If the heights of the potential barriers are distributed according to a normal distribution, then

$$\alpha'_V = \frac{\bar{\Lambda}^2 N_V}{4 \pi \rho s^3 k_B T (\Delta V^2)^{1/2}} \times \int_{-\infty}^{+\infty} \exp \left[- \frac{(V - \bar{V})^2}{2(\Delta V^2)} \right] \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} dV. \quad (17)$$

The integral (17) is usually calculated numerically, and agreement with experiment is achieved by adjusting the parameters of the distribution—the mathematical expectation \bar{V} and the variance ΔV^2 .

In order to determine the characteristic experimental manifestations of the structure of the amorphous material, resulting in a distribution of the barriers around some average value \bar{V} , we assume that the barriers are distributed uniformly over a range of values $V_{\max} = \bar{V} + (\Delta V/2)$ and $V_{\min} = \bar{V} - (\Delta V/2)$.

Then

$$\alpha'_V = \frac{\bar{\Lambda}^2 N_V \omega}{2 \rho s^3 \Delta V} \times \arctan \frac{\omega \bar{\tau} [-\exp(-\Delta V/2k_B T) + \exp(\Delta V/2k_B T)]}{1 + \omega^2 \bar{\tau}^2}, \quad (18)$$

where $\bar{\tau} = \tau_0 \exp(\bar{V}/k_B T)$.

If $\Delta V/k_B T < 1$, then making a series of expansion of the exponential and the inverse tangent, we obtain

$$\alpha_V \approx \frac{\bar{\Lambda}^2 N_V}{2\rho s^3 k_B T} \left[\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} + \frac{(\Delta V) \omega^2 \tau}{2k_B T} - \frac{(\Delta V)^2 \omega^4 \tau^3}{8(k_B T)^2} + \dots \right]. \quad (19)$$

The last relation shows that if α is observed to have a peak in amorphous metals, then by measuring the asymmetry of the peak at high frequencies it is possible to estimate the spread in the potential barriers. We note in passing that the relation (19) shows, in agreement with experiment, that in the case when there is a distribution of barrier heights $\alpha(\omega)$ differs from the case $\Delta V = 0$ only at high frequencies.

In the opposite limiting case $\Delta V \gg k_B T$ and retaining only the first two terms of the expansion, we have

$$\alpha_V = \frac{\pi \bar{\Lambda}^2 N_V \omega}{4\rho s^3 \Delta V} \left\{ 1 - \left[\frac{\omega \tau \exp(\Delta V/k_B T)}{1 + \omega^2 \tau^2} \right]^{-1} \right\}, \quad (20)$$

i.e., to a first approximation α does not depend on the temperature and is proportional to the frequency. When the next terms of the expansion are included, α decreases somewhat with increasing T . The formulas (16)–(20) describe qualitatively, and even quantitatively if the parameters are suitably chosen, the existing experimental results on the acoustic properties of metallic glasses. Thus, depending on the relaxation mechanism and the form of the distribution of the heights of the potential barriers, the frequency dependences of α can range from $\alpha \sim \omega^{-1/2}$ to $\alpha \sim \omega^2$. The frequency range investigated in metallic glasses is bounded above by $\omega_b \approx 10^9$ Hz. Relaxation maxima have been observed in the above-noted cases of hydrogenated glasses or Gorski's relaxation. In the other cases $\alpha \sim \omega^2$, indicating that comparatively narrow distributions of the potential-barrier heights, for which $\omega \tau < 1$, are realized in metallic glasses. Especially weak sound absorption can arise in the case of a normal distribution of barrier heights [see Eq. (17)], when the most effective barrier heights V_{eff} , giving a maximum of the function $\omega \tau / (1 + \omega^2 \tau^2)$, are unlikely, i.e.,

$$[\bar{V} - k_B T \ln(\omega \tau_0)] \geq 3(\bar{V}^2)^{1/2}.$$

It is this case that was probably observed in Ref. 38 in the metallic amorphous alloy $\text{Pd}_{0.795}\text{Ag}_{0.04}\text{Si}_{0.165}$, in which in the frequency range 60–500 MHz it was found that α for longitudinal and shear waves is very small and less than in fused quartz. From this standpoint it is understandable why increasing the Ag concentration by a factor of 1.5 did not change the sound absorption within the limits of the error of measurements.

Therefore, in this alloy the thermoelastic losses associated with heat conduction are the main source of sound absorption.

Replacing Ag atoms by Cu or Ni atoms with the same concentration increases α by factors of 7 and 10, respectively. Since such low Cu or Ni concentrations cannot change the thermoelastic losses in a metal so strongly, the observed increase can be attributed to the contribution of relaxation by one of the mechanisms considered above. The quadratic frequency dependence of α indicates that, as in the case of

Ag, relaxation with a single transition through a potential barrier predominates. Since the atomic and ionic radii of Ag, on the one hand, and Cu and Ni, on the other, differ by 10%, it is unlikely that the deformation potential will change much. Therefore, experimentally, the relaxation time increases by at least an order of magnitude, i.e., the height of the potential barrier to the translational motion of the atoms [see Eq. (17)] must increase substantially.

According to acoustic experiments, however, as long as the condition $\omega \tau < 1$ is satisfied, only the combination $\bar{\Lambda}^2 \tau N_V$ can be determined. For this reason, in such cases all estimates are unreliable, if there is no additional information that can be brought to bear on the problem. Thus, for the alloy $\text{Pd}_{0.775}\text{Cu}_{0.06}\text{Si}_{0.165}$, setting $\tau_0 = 10^{-13}$ sec and taking into account the fact that $\alpha \sim \omega^2$ right up to frequencies of 500 MHz, we obtain the estimate $\bar{V} < 0.1$ – 0.2 eV. If, next, it is assumed that all Cu atoms participate in the relaxational process, then $(\bar{\Lambda}^2)^{1/2} \approx 1$ eV.

In this sense experiments in a wide range of frequencies and temperatures, which make it possible to check the theoretical models qualitatively, are of greatest interest. Thus experiments on the same metallic amorphous alloys performed in a wide temperature range have shown that for $T > 150$ – 200 K α starts to increase with temperature, though the quadratic frequency dependence of α remains. It is easy to see that in none of the models with $\alpha \sim \omega^2$ considered above does α increase with temperature.

The simplest assumption that makes it possible to change the temperature dependence of α is the assumption that different potential wells have not only different deformation potentials but also different depths, i.e., the potential barrier is asymmetric.

If, as before, single transitions through a barrier are considered, then each pair of wells must be regarded as isolated. It is obvious that the distribution of atoms over the wells is, like the amorphous state itself, a thermodynamically nonequilibrium distribution. However, the equilibrium distribution of atoms within wells of the same kind with the energies at the bottoms differing by Δ_w satisfies the equation

$$N_{\Delta_w}^{(1)} / N_{\Delta_w}^{(2)} = A_{21} / A_{12} = \exp(\Delta_w / k_B T), \quad (21)$$

where $N_{\Delta_w}^{(1)}$ and $N_{\Delta_w}^{(2)}$ are the number of atoms on opposite sides of the potential barrier and A_{21} and A_{12} are the probabilities of a transition through the potential barrier V from different wells of the pair.

An elastic wave, modulating the transition probabilities δA_{12} and δA_{21} due to deformation interaction, disrupts the distribution of atoms δN_{Δ_w} in the potential wells of the pairs. For wells whose depths differ by Δ_w the balance equation has the form

$$\begin{aligned} \dot{N}_{\Delta_w}^{(1)} = & - (A_{12} + \delta A_{12}) (N_{\Delta_w}^{(1)} + \delta N_{\Delta_w}^{(1)}) \\ & + (A_{21} + \delta A_{21}) (N_{\Delta_w}^{(2)} + \delta N_{\Delta_w}^{(2)}). \end{aligned} \quad (22)$$

Since for isolated pairs $\delta N_{\Delta_w}^{(1)} = \delta N_{\Delta_w}^{(2)}$, and carrying out the standard calculation of α_{Δ_w} ,¹ we find for these pairs

$$\alpha_{\Delta} = \frac{\Lambda_{\Delta}^2 N_{\Delta}}{4\rho_0^3 k_B T \text{ch}^2 (\Delta_w / 2k_B T)} \frac{\omega^2 \tau}{1 + \omega^2 \tau^2},$$

$$\tau = \frac{1}{2} \tau_0 \left(\exp \frac{V}{k_B T} \right) \text{ch}^{-1} \frac{\Delta_w}{2k_B T}. \quad (23)$$

The general sound absorption coefficient is found by summing over all wells with the corresponding distribution functions. If it is assumed once again, for simplicity, that Λ_{Δ} , V , and Δ_w are independent random variables, then

$$\alpha_{\Delta} = \alpha_V k_B T / M_{\Delta}, \quad (24)$$

where

$$M_{\Delta} = \int_{-\infty}^{\infty} G_4(x) \frac{dx}{\text{ch}^2 x}.$$

Here $G_4(\Delta_w)$ is the distribution function of the probabilities of energy asymmetry of the wells. If, for example, the asymmetry distribution is uniform and $\alpha_V = \alpha'_V$, then the total sound absorption coefficient is proportional to the temperature. By combining the distribution functions $G_4(\Delta_w)$ and the different expressions (17) and (20) for α_V we can approximate the experimental temperature dependences obtained for the acoustic parameters for different alloys (the sound speed is calculated for the relaxation processes in the standard manner¹ from the known values of α). The temperature and frequency dependences of α obtained in amorphous semiconductors and dielectrics are mainly similar to the dependences considered above for amorphous metals.^{34,36,39-41} The frequency dependences of α in different temperature ranges can vary from ω^0 to ω^2 ; one observes either maxima of α as a function of the temperature much wider than the Debye peaks or α is at first temperature independent and then, at higher temperatures but still far from the vitrification point, α increases with temperature.

As the discussion presented in Ref. 34 shows, these experiments on sound absorption can be interpreted on the basis of relaxation processes with a single transition through the barriers between symmetric potential wells, choosing a suitable distribution of the potential-barrier heights. It is assumed that at low temperatures the transitions through the barriers occur by means of tunneling and that at high temperatures the barriers are overcome by an activation over-barrier process.

Big problems arise in any attempt to determine which of the structural units of amorphous semiconductors or dielectrics participate in the translational motion. Thus, for example, in Ref. 42 it is concluded, only on the basis of the differences in the experimentally determined numerical values of the activation energy, that in As_2S_3 at low temperatures the S atoms, which are much more weakly bound with two As atoms than in the $S-As-S$ bond, undergo tunneling transitions, while at temperatures $T > 140$ K the complex AsS_3 makes a transition over the barrier.

Another typical example are the models proposed for specifying the relaxation process observed experimentally in SiO_2 .

Some approaches employ motion of oxygen atoms in Si-O-Si complexes in a transverse direction with respect to

the bonds,⁴³ other approaches employ motion along the bonds,⁴⁴ and still other approaches employ the hypothesis of fused quartz as a double structure in the form of a mixture of two types of octahedra, corresponding to the α and β phases of crystalline quartz.⁴⁵ The first two models do not agree well with the x-ray diffraction data, while in the last model it is possible to adjust the concentration of the phases so that the x-ray scattering and the temperature dependence of the sound speed are correctly described.

However, it is quite difficult to specify the relaxational mechanism on the basis of only acoustical measurements. The same situation exists in the case of measurements of α and s in amorphous elemental semiconductors.

In a-Si, aside from a relaxation maximum associated with dissolved hydrogen, there is also observed³⁹ another peak in α , which is attributed in Ref. 39 to the breaking of one of the weakened bonds of the silicon atoms and saturation of another bond, so-called bond switching. The activation energy of the relaxation process, as determined from the temperature shift of the maximum at different frequencies, was found to be 1.73 ± 0.2 eV, though the energy required to break one bond is 1.15 eV. According to Ref. 39, this excess energy goes into deformation of the remaining three bonds.

In principle, defects of the type of unpaired "dangling" bonds are quite typical for amorphous silicon and germanium prepared by evaporation in vacuum or sputtering, since directed covalent bonds, as noted above, hinder relaxation. According to EPR data for the samples investigated, the concentration of unpaired spins was $6 \cdot 10^{19} \text{ cm}^{-3}$. However, since methods for preparing amorphous silicon with a low concentration of "dangling" bonds do exist, this contribution can, in principle, be separated.

The question of the possibility of observing in amorphous semiconductors the contribution of electrons (holes) to sound absorption is of great interest. In the absence of the piezoelectric effect, any interaction of electrons with the elastic wave occurs via the deformation potential. As noted in Ref. 1, such an interaction at realistically attainable frequencies (up to 10^9 – 10^{10} Hz) is much weaker than the piezoelectric interaction, and α on unlocalized carriers does not exceed fractions of a dB/cm, and this makes it impossible to separate it from the different mechanisms associated with defects. An effective method for separating the deformation interaction of sound and unlocalized electrons in crystalline semiconductors was doping, which, as is well known, in the case of amorphous semiconductors had a weak effect on the electric properties. Experiments on separation of this contribution could probably also be based on investigation of the dependence of α on the pulling electric field, which produces drift of charge carriers.

Localized electrons (holes) can, in principle, make a contribution to sound absorption of the same order of magnitude as the piezoelectric effect contribution in crystalline weakly doped semiconductors (see Ref. 1). This is associated with the possibility of the existence of nearby (separated by less than the average distances) centers of localization which have different deformation potentials. If, as before, we denote by Λ_{mn} the difference of the deformation potentials of two neighboring centers m and n , then the intensity E of the electric field produced will be of the order of $\Lambda_{mn} / q_e r_{mn}$, where q_e is the electron charge and r_{mn} is the distance between the centers. This electric field modulates the proba-

bilities of transitions of a localized carrier between centers of localization, which gives rise to relaxation absorption of sound. Transitions can evidently occur between centers by means of tunneling as well as over-barrier transitions. As mentioned above, tunneling through a barrier was studied in detail in Ref. 46 for both weakly doped and amorphous semiconductors. This contribution to the sound absorption coefficient can be separated by applying a magnetic field (see the review and bibliography in Ref. 42), which, by transforming the wave function of a localized carrier, changes α . Such experiments, performed in Ref. 42, show that in the chalcogenide glassy semiconductor (CGS) α -As₂S₃ α does not depend on the intensity H of the magnetic field. From this it was concluded that electrons do not contribute to α .

We note, however, that if transitions between centers of localization are over-barrier transitions, then the effect of the transformation of the wave function on sound absorption is substantially weaker, and the absence of a field dependence $\alpha(H)$ could indicate not that sound absorption by localized electrons does not occur but rather that the potential barrier is overcome by an over-barrier process. Moreover, there exists an entire series of experimental results in CGS (see review and bibliography in Ref. 48)—photoluminescence, ac conductivity, and others—which can be understood if it is assumed that over-barrier transitions occur in pairs of defects C^+ and C^- , where C^+ and C^- denote atoms of the chalcogen with positive or negative charges. Due to the Coulomb interaction, they can form close pairs with variable valence. For this reason, we estimate the contribution of localized carriers (for definiteness electrons) to sound absorption. This can be done by repeating the arguments presented above and taking into account the fact that in the case of the formation of a close pair spatial overlapping of the potentials of each center is possible. As a result, the height of the potential barrier now depends on the distance between the centers [otherwise α is calculated from Eq. (23)]. However, we employ the results of Ref. 48, where the ac electric conductivity in CGS, due to an over-barrier transition in one close pair of variable valence, is calculated:

$$\operatorname{Re} \sigma_n(\omega) = \frac{q_p q_c r_{mn}^2 \omega}{12k_B T \operatorname{ch}^2(\Delta_w/2k_B T)} \frac{\omega \tau}{1 + \omega^2 \tau^2}; \quad (25)$$

Here, τ is determined by the relation (23), and q_p and q_c are the electric charges of the pair and localized carrier, respectively.

The energy lost by the elastic wave per unit time can be calculated from the Joule-Lenz law:

$$W_n = \frac{\Lambda_{mn}^2 \omega^2 \tau}{12k_B T \operatorname{ch}^2(\Delta_w/2k_B T) (1 + \omega^2 \tau^2)}. \quad (26)$$

The sound absorption coefficient is found as the ratio of the energy dissipated per unit volume by all pairs to the energy of the elastic wave. Repeating the arguments of Ref. 48, made in order to find the hopping over-barrier electric conductivity, we obtain the following expression for α :

$$\alpha_V = \left(\frac{4q_p q_c}{\epsilon V_{\max}} \right)^3 \frac{\pi^2 \Lambda_{mn}^2 N_p N_b \omega^a}{9\rho_s^3 V_{\max} \cdot 2^a \tau_0^c \sin(\pi a/2)}, \quad (27)$$

where

$$a = 1 - c, \quad c = 4k_B T / V_{\max},$$

$$b = \frac{2k_B T}{\Delta_0} \int_0^{\Delta_0/2k_B T} \frac{dx}{\operatorname{ch}^2 - c_x},$$

N_p is the number of singly filled pairs of variable valence, N is the total number of defects, and ϵ is the dielectric permittivity.

In the derivation of the formula (27) the distribution of the energy asymmetry of the wells was assumed to be uniform:

$$G_4(\Delta_w) = H(\Delta_0 - |\Delta_w|)/2\Delta_0, \quad (28)$$

and the distribution of the distances between the centers of the pairs was assumed to be uncorrelated:

$$G_2(r_{mn}) = 4\pi N r_{mn}^2 \exp\left(-\frac{4\pi}{3} N r_{mn}^3\right). \quad (29)$$

The overlapping of the potential wells in the region between the centers was taken into account by lowering the potential barrier V :

$$V_{\max} - V = 4q_p q_c / \epsilon r_{mn},$$

where V_{\max} is the barrier height in the absence of overlapping. In addition, for the averaging it was assumed that⁴⁸

$$\begin{aligned} r_{mn}^2 dr_{mn} &= \left(\frac{4q_p q_c}{\epsilon V_{\max}} \right)^3 \left(1 - \frac{V}{V_{\max}} \right)^{-4} \frac{dV}{V_{\max}} \\ &\approx \left(\frac{4q_p q_c}{\epsilon V_{\max}} \right)^3 \left(\exp \frac{4V}{V_{\max}} \right) \frac{dV}{V_{\max}} \end{aligned}$$

and

$$\exp\left(\frac{4\pi}{3} N r_{mn}^3\right) \approx 1,$$

which corresponds to the assumption that pairs of centers separated by a distance less than the average distance between the centers in the system make the main contribution to the conductivity and sound absorption coefficient.

Taking into account the Coulomb correlation in the arrangement of pairs of centers, which reflects the specific nature of the technology employed for preparing the amorphous semiconductor, results in a being replaced by a' given by⁴⁸

$$a' = 1 - c + (T/4T_g),$$

where T_g is the glass-formation temperature, at which a transition from the highly elastic state into the standard amorphous state occurs and the diffusion coefficient decreases sharply.

A characteristic experimental indication of the contribution of localized charge carriers is that as the temperature increases, the frequency dependence $\alpha(\omega)$ becomes sublinear. In addition, as observed experimentally, the absorption

coefficient α can depend on the frequency. For pair concentrations not less than 10^{19} – 10^{20} cm $^{-3}$ and $V_{\max} \approx 1$ – 2 eV, α is of the order of several dB/cm.

It is nonetheless clear that the question of whether different charge carriers (electrons, holes, ions) or structural complexes make the determining contribution in amorphous semiconductors has still not been resolved.

Similar results are obtained if the potential energy of an ion in certain regions of a disordered matrix has the form of a curve with two minima of equal depth.

More precise arguments can often be made in the case of amorphous dielectrics—glasses, in spite of their very complicated composition. This is connected with the possibility of purposefully changing the concentration of some structural units and measuring the acoustic characteristics as a function of the frequency and temperature for different compositions. Thus detailed investigations of glasses with the composition $(\text{AgI})_x [(\text{Ag}_2\text{O})_y (\text{B}_2\text{O}_3)_{1-y}]_{1-x}$, in which either $x = 0$ and y ranges from 0 to 0.33 or $0 < x < 0.7$ and $0.25 < y < 0.5$, were investigated in detail at frequencies of 5–45 MHz and temperatures 80–460 K.

It was found that sound absorption increases with both increasing x and increasing y , i.e., sound absorption is determined by the silver atoms (ions) in the glass. The sound absorption coefficient α as a function of temperature is observed to have peaks whose width increases with decreasing y , so that at concentrations $y \approx 0.1$ the temperature dependence of α is no longer discerned. In regions where the peaks in α can be seen clearly, it is possible to find, in accordance with Eq. (17), parameters of the Gaussian distribution of the barrier heights for which agreement with experiment is attained. Typical values of the deformation potential were found to be several tenths eV and the parameters of the distribution are as follows: \bar{V} is several tenths eV/mole and $(\bar{V}^2)^{1/2}$ is several hundredths eV/mole.

It was also established that the parameters of the distribution of the potential barriers depend on the concentration of silver ions. Thus, for example, for $y = \text{const}$ and $x = 0.3$ $\bar{V} = 0.385$ eV/mole and for $x = 0.7$ $\bar{V} = 0.25$ eV. At the same time the standard deviations of the heights of the potential barriers decrease with increasing Ag concentration. For example, for $x = 0.4 = \text{const}$, as y increases from 0.2 to 0.5 the parameter $(\bar{V}^2)^{1/2}$ decreases from 0.11 to 0.05 eV/mole or in the case $y = 0.5 = \text{const}$, as x decreases from 0.7 to 0.3 the parameter $(\bar{V}^2)^{1/2}$ decreases from 0.057 to 0.033 eV/mole.

Another detailed investigation of the acoustic properties of complex glasses was performed in Refs. 34 and 37, where the sound absorption coefficient and sound speed were measured in niobium-phosphate glasses of the system $(\text{M}_2\text{O})_x (\text{P}_2\text{O}_5)_y (\text{Nb}_2\text{O}_5)_{1-x-y}$. The metal M was one of Li, Na, K, and Rb. The temperatures ranged from 200 to 400 K; α was measured at frequencies in the range 200–1500 MHz; and, s was measured at 30 MHz.

It was found that in all glasses except lithium glasses $\alpha \sim \omega$ and is virtually temperature independent. Conversely, the sound absorption coefficient in lithium glasses varies nonmonotonically as a function of the temperature, reaching very large values (up to several hundreds dB/cm at $\omega/2\pi = 400$ MHz). As the temperature decreases, α in lithium glasses decreases rapidly and at $T \approx 100$ K sound absorption

in them is equal to that in the other glasses which were investigated.

In order to take into account the frequency and temperature dependences of α in glasses which do not contain lithium, the experiment of Ref. 34 was analyzed using the model of single transitions through barriers with uniformly distributed heights. At low temperatures it was assumed that the barrier is overcome by tunneling, and for $T \gtrsim 100$ K the barrier is overcome by an over-barrier transition. It was found that this wide temperature range of measurements of α could be described by using the same values of the parameters: $\Lambda = 1.2$ eV, $V_{\max} > 0.3$ eV, $V_{\min} < 0.02$ eV, and $N/\Delta V = 6 \cdot 10^{45}$ J $^{-1}$ m $^{-3}$, indicating that the model was chosen successfully.

Measurements of the sound speed in the same phosphate glasses $(\text{Rb}_2\text{O})_{0.35} (\text{Pb}_2\text{O}_3)_{0.35} \cdot (\text{Nb}_2\text{O}_5)_{0.3}$ at 30 MHz also showed that when the same values of the adjustable parameters as those found for the sound absorption coefficient are used, the low-temperature behavior of s can be explained with the help of the model of a single transition through the barriers. At high temperatures, however, the experiment cannot be explained by such a relaxation mechanism, since higher values of TCS are required. The detailed analysis performed in Ref. 37 shows that in these glasses at high temperatures the anharmonicity, described within Akhiezer's theory,⁴⁹ can make the main contribution to the TCS.

Since the introduction of lithium into the glass increases α and also causes the functions $\alpha(\omega)$ and $\alpha(T)$ to be non-monotonic, this indicates that an additional mechanism in sound absorption must be taken into account. As shown in Ref. 34, the experimental results can be described well by using the sum of two normal distributions of the relaxation times:

$$G_3(V) = \frac{1}{\sqrt{2\pi}} \left\{ \frac{N_1}{(\bar{V}_1^2)^{1/2}} \exp \left[-\frac{(V - \bar{V}_1)^2}{2\bar{V}_1^2} \right] + \frac{N_2}{(\bar{V}_2^2)^{1/2}} \exp \left[-\frac{(V - \bar{V}_2)^2}{2\bar{V}_2^2} \right] \right\},$$

$$N_1 + N_2 = N, \quad (30)$$

where $N_1/N \approx 0.2$, α as a function of the lithium concentration $(\bar{V}_1^2)^{1/2}$ ranges from 0.085 to 0.037 eV, $(\bar{V}_2^2)^{1/2}$ ranges from 0.07 to 0.035 eV, $\bar{V}_1 = 0.19$ eV, and \bar{V}_2 falls in the range 0.35–0.325 eV.

Thus, just as in the case of silver, as the concentration of lithium ions increases, the height and variance of the potential barriers to translational motion also decrease. The fact that the potential barriers manifested in acoustic experiments are associated with the translational motion of ions was demonstrated experimentally in Ref. 34 by measurements of the electric conductivity at low frequencies as a function of the temperature in lithium-phosphate glasses simultaneously with measurements of α . It was found that in both cases the barrier heights are very close: At different lithium concentrations the difference does not exceed 0.020–0.015 eV and depends in exactly the same manner on the concentration of lithium ions. Since in Ref. 34 the measurements of the electrical conductivity were performed at 1000

Hz, they correspond to the condition $\omega\tau' \ll 1$, where τ' is the time of a single hop. In this case the activation energy of electrical conductivity is equal to the percolation level V_{per} of the system. It is well known²⁴ that for a normal barrier-height distribution the difference between the percolation level and the average barrier height is $V_{\text{per}} - 0.8(\bar{V}^2)^{1/2}$, i.e., within the limits of experimental error, the percolation level is equal to the activation energy found from α . For this reason, it can be regarded as an established fact that the excess sound absorption by Ag and Li ions in glasses is associated with a single transition through potential barriers.

We now discuss how the concentration of lithium and silver ions affects the parameters of the potential relief.

We note first that within the model of a glass in the form of a collection of double potential wells separated by potential barriers with some kind of distribution of the barrier heights, the only effects of the concentration of mobile Li and Ag ions are that the number of filled wells increases and α increases in proportion to the ion concentration. For this reason, such an effect, first, could be associated with the dissolved Li or Ag creating its own potential relief. If, however, the wells are assumed to be so wide that many of the introduced atoms can fall into them and the process of ions falling into potential wells of width R_w is assumed to be random, then the fluctuations in the number of atoms in a well and hence also the disturbances of the potential relief are determined by $(N_{\text{tr}} R_w^3)^{1/2}$, where $(N_{\text{tr}} R_w^3) \gg 1$ and N_{tr} is the concentration of mobile ions, i.e., in contradiction to experiment, the fluctuations grow with increasing N_{tr} .

Second, if the characteristic widths R_w of the potential wells are such that the wells can accommodate small-scale fluctuations (the characteristic width $R_m \ll R_w$), then when Li or Ag ions are introduced the deepest wells are filled first (compare the energy structure of strongly doped semiconductors). Therefore, the potential barriers which ions must overcome in order to participate in translational motion are high and their variance is greatest for small N_{tr} . It is easy to see that in agreement with experiment both \bar{V} and $(\bar{V}^2)^{1/2}$ decrease as N_{tr} increases.

In this situation, it is no longer adequate to adjust the parameters of the barrier height distribution in accordance with Eq. (17) or (30) in order to describe the experimental dependences $\alpha(\omega)$ and $\alpha(T)$, since the condition

$$\int_0^{V_b} g_s(V) e^{-V/k_B T} dV = N_{\text{tr}} R_w^3 \quad (31)$$

must also be satisfied, where V_b is the maximum energy of the filled small-scale fluctuations and $g_s(V)$ is the corresponding density of states in a potential well with characteristic spatial width R_w and depth V_1 . It is easy to see that potential barriers to translational motion range from V_1 to $V_1 - V_b$. For this reason, it should also be possible to extract information about the density of states, produced by fluctuations in the main network of the glass, from ultrasonic measurements.

Aside from the above-enumerated parameters of an amorphous structure, in Ref. 36 the constant τ_0 appearing in the expression for the relaxation time was also determined and found to be $\approx 10^{-14}$ sec.

We have already mentioned¹ that the values of τ_0 of the order of 10^{-14} – 10^{-15} sec and less, found from acoustic measurements, are questionable, since estimates obtained from measurements of the temperature positions of the maxima of the sound absorption coefficient at different frequencies are not accurate enough. Thus, if

$$\omega_1 \tau_0 \exp(V/k_B T_1) = \omega_2 \tau_0 \exp(V/k_B T_2) = 1, \quad (32)$$

where T_1 and T_2 are the temperatures of the maxima at frequencies of ω_1 and ω_2 , then for $V = V_0 - \text{const} \cdot T$ we obtain, under the condition (32), an estimate for τ_0 by a factor $\exp(\text{const}/k_B T)$. For example, in order that τ_0 be 10^{-13} sec, $\text{const} \cdot T$ at $T = 300$ K must not exceed 0.06 eV, which for typical potential barriers of several tenths eV is at the level of the measurement errors.

In conclusion, we note that the overwhelming majority of the existing experimental results for amorphous media at high temperatures can be described, at least formally, using a model of over-barrier transitions of atoms or ions, which at high temperatures replace tunneling. However, there exist other approaches for describing relaxation processes in glasses at high temperatures on the basis of improved TLTS models. These models include two-phonon⁵⁰ and multi-phonon processes⁵¹ as well as the model of quasilocal harmonic vibrations.^{52,53}

1.2. Monatomic melts

In spite of the great success achieved in the study of the structure of liquids with the help of direct methods (scattering of x-rays and thermal neutrons), combined with molecular-dynamics modeling and in questions concerning the structure of liquids and organization of thermal motion, much remains unclear and this has stimulated the use of a large number of model approaches, which are, as a rule, effective for explaining one or two physical properties, but are of little use for other properties.

Under these conditions it is important, as in the past, to accumulate more experimental data on the properties of liquids in a wide range of external conditions and, on the one hand, to bring out consistent laws and, on the other, to compare these laws with estimates obtained from different theoretical approaches.

We now examine from this standpoint the accumulated experimental data on the speed and absorption of elastic waves in monatomic melts of metals, semimetals, semiconductors, and dielectrics.

This choice of objects of study is dictated by, aside from their relative structural simplicity, the two following circumstances. First, they have all been studied many times with the help of direct methods (see the reviews Refs. 54–58) in a wide temperature range. Second, other structure-sensitive physical characteristics have been investigated in detail for these objects,⁵⁹ and this makes it possible to determine the place of acoustic methods of investigation of the structure of liquids among other indirect methods.

In attempts to separate the role of order or disorder as well as the effect of the character of the thermal motion in the acoustic characteristics, by no means a trivial question is which characteristic should be compared for substances in the amorphous crystalline and melted states. It is obvious that the propagation speed of longitudinal waves for these

purposes unsuitable, though it is this quantity that is, as a rule, employed for estimating the changes in the elastic properties of a material which are associated with the transition into the liquid state. This is because the expression for the speed of longitudinal waves in crystals contains the elastic moduli which are associated with shear deformations, while in the case of amorphous materials $4G/3$ enters directly. In liquids, however, with shear viscosity of several centipoise (which is typical for most of the melts studied) $G \approx 0$ for all realistically attainable frequencies (the shear modulus relaxation time τ_η is of the order of η'/K'_τ , where η' is the coefficient of shear viscosity and $(K'_\tau)^{-1}$ is the part of the bulk modulus of the liquid that is connected with the translational motion of the atoms).

For this reason, it is desirable to characterize, as done above, the equilibrium elastic properties and the change in these properties on melting by the bulk modulus K' , which describes the change in volume under hydrostatic compression in both the solid and liquid states. From the viewpoint of the characteristics of the internal structure of the melt, however, the absolute quantity K is uninformative. For example, lead and germanium melts, which have completely different structure and physical properties, have close bulk moduli: $3.53 \cdot 10^{11}$ and $3.57 \cdot 10^{11}$ dynes/cm², respectively, while copper and silver melts, which have very close properties, have substantially different bulk moduli: $9.56 \cdot 10^{11}$ and $6.8 \cdot 10^{11}$ dynes/cm². In this sense, checking the theoretical approaches by comparing with experiment the computed values of K or s_l , of course, as is often done, does not reveal the characteristic structural features of the melts. As will become evident from what follows, the temperature coefficient of the bulk modulus $K^{-1} dK/dT$ (TCB) is a very subtle physical characteristic of the melt and is sensitive to manifestations of different types of ordering.⁶⁰ As in the case of amorphous materials, by ordering in a liquid we mean processes which reduce the number of possible microstates of the system, i.e., reduce the entropy of the system.

As far as the sound absorption coefficient is concerned, it is well known³² that there arises in liquids additional (as compared with solids) sound absorption associated with momentum transfer due to shear viscosity. At frequencies ω such that $\omega\tau_\eta \ll 1$, this sound absorption coefficient α_η is proportional to the viscosity and the squared frequency and does not carry any additional information as compared with direct measurements of η' . In addition, as before, heat conduction contributes to the sound absorption coefficient. This mechanism of absorption in liquids α_κ does not have any peculiarities as compared with crystals.¹ Its relative contribution to the total sound absorption in melted metals and semimetals, however, is large due to the fact that α is small in these substances as compared with the crystalline state. For this reason, both contributions are usually subtracted from the experimental value α_{exp} .

The excess sound absorption coefficient α_m computed in this manner is related with "internal" relaxational processes and it can be expected that different types of structural processes, in particular ordering, will be manifested in it. The problem for most melts of metals, semimetals, and semiconductors that have been studied is that α_m is found as a small difference of two large numbers. In addition, $\alpha_\eta + \alpha_\kappa$ contains all errors in measurements of η' , κ , ρ , and s_l , constituting up to 10%, and as a result, the experimental manifesta-

tation of relaxation processes in the sound absorption coefficient in melts of metals can itself often be established only by analyzing the temperature dependences of α_{exp} on the one hand and $\alpha_\eta(T) + \alpha_\kappa(T)$ on the other.⁶¹ It is not difficult to show that for most melts the latter sum increases with increasing temperature no more rapidly than in proportion to T . Indeed, for low-viscosity liquids ($\omega\tau_\eta < 1$) $\alpha_\eta \sim \eta'$ and it decreases with increasing T ;⁵⁹ $\alpha_\kappa \sim \kappa T$ (Ref. 1) for fused metals increases as $\sim T$, since $\kappa \approx \text{const}$ and for dielectrics $\kappa \sim 1/T$. For this reason, the relaxation contribution to the sound absorption coefficient and to the equilibrium bulk modulus K_0 must be determined individually for each melt using the relations

$$\begin{aligned}\alpha_m &= \alpha_{\text{exp}} - \alpha_\eta - \alpha_\kappa \\ &= \alpha_{\text{exp}} - \frac{\omega^2}{2\rho s^3} \left[\eta' + \kappa \left(\frac{1}{C_V} - \frac{1}{C_P} \right) \right],\end{aligned}\quad (33a)$$

$$K_{\text{exp}} = \rho s_{\text{exp}}^2 \approx K_S \left(1 - \frac{2\alpha_m s_{\text{exp}}}{\omega^2 \tau} \right), \quad (33b)$$

where C_V and C_P are the heat capacities at constant volume and constant pressure, s_{exp} is the experimentally determined propagation speed of elastic waves, and K_S is the instantaneous bulk modulus at constant entropy, i.e., in the absence of relaxation processes. In deriving Eq. (33b) we employed Eq. (1) and the fact that $\Delta s/s < 1$.

In melts of group I metals (Cu, Ag) and alkaline-earth metals the difference between the heat capacities C_V and C_P can reach 40%, so that the adiabatic bulk moduli K_S must be distinguished from the isothermal bulk moduli K_T . Since at all frequencies employed for investigating the melts the process of propagation of elastic waves is adiabatic, in what follows, unless otherwise stated, K is the adiabatic modulus.

In order to extract information about the organization of order or disorder and thermal motion in simple (monatomic) liquids, we consider two aspects of the results of acoustic experiments: a) How does melting, i.e., acquisition by atoms of translational freedom (dynamical disorder) as compared with static disorder (amorphous state) and the ordered crystalline state (near melting), affect the elastic properties of the materials? b) Which properties are manifested in the temperature behavior of the bulk modulus and the sound absorption coefficient in melts of substances with different types of short-range order and interatomic interaction forces?

In other words, only the change in the acoustic properties of the substances either under melting or as a function of external factors need be discussed. Even in this formulation, however, it is difficult to interpret unequivocally the results of acoustic experiments. This is primarily because in all metallic melts and in most semiconductor melts the condition $\omega\tau \ll 1$ ($\alpha \sim \omega^2$) is realized in high-temperature experiments and, therefore, τ cannot be found directly. For this reason, τ is estimated with the help of more or less plausible theoretical hypotheses, so that there is some arbitrariness in the values of K calculated from Eq. (33b). In addition, as a consequence of the weakness of the theory of the liquid state, detailed models of relaxation processes in monatomic liquids that could contribute to the experimentally observed values of α_m have not been developed.

In this situation, in order to analyze the manifestations of order or disorder in acoustic properties we eschew the results obtained by direct methods of studying the structure of liquids.

In Ref. 1 it was already mentioned that even using molecular-dynamics modeling it is still impossible to draw an unequivocal conclusion about the details of the structure of the liquid from diffraction data. For this reason, melts are probably best classified only on the basis of experimentally observed properties as functions of the radial distribution or structure factors, without assigning them any specific physical meaning. Such a systematization, performed in Ref. 62, for liquid metals, semimetals, and elemental semiconductors has made it possible to divide all investigated melts into three groups. The first group contains alkali, alkaline-earth, precious, 3d, and rare-earth metals, Al, In, Tl, Pb, Pd, Pt, and Zr. The structure factors of these metals have a symmetric maximum, and the functions $g(r)$ are described well by the hard-sphere model. The second group consists of bivalent Zn, Cd, and Hg, in which the first peak of the structure factor near the melting points has distinct asymmetry. The third group consists of elements whose main feature is that the volume decreases on melting—Ga, Sb, Bi, Si, Ge, and also Sn. In the case of these metals, a secondary peak is observed on the high-angle side of the peak in the structure factor. As the diffraction experiments show, these features in the structure factors vanish with increasing temperature.

Already the first classifications of the acoustic properties of metallic melts^{60,61} showed that melts fall into similar groups according to the temperature coefficients of the speed of sound. The behavior of s as a function of the temperature was later studied many times and different authors obtained largely the same results. The experimental results obtained on the absolute values of s differ by several percent, which is not significant for the purposes of our discussion, and the results on the TCS are quite close. For this reason, we do not present here the existing bibliography on this question, and we employ the experimental results obtained in Refs. 60 and 61 by a universal method and on the same apparatus, with the exception of new data which have appeared

(anyone interested in a more detailed discussion of this question can obtain additional information from Refs. 59–61). The temperature dependences of the sound absorption coefficient have been studied in much less detail, though without these data it is impossible to estimate, in accordance with Eq. (33b), the equilibrium bulk modulus. For this reason, we focus our attention on melts for which the temperature dependences $\alpha(T)$ and $s(T)$ are known in a wide range of temperatures.

1.2.1. Acoustic properties of the melts of typical metals

The typical temperature dependences of α and s for close-packed metals from the first group are presented in Fig. 2 using the example of Pb.⁶³

Analogous temperature dependences are observed for indium and thallium melts.^{64,65} For these melts s_{exp} decreases linearly and α_{exp} increases monotonically with increasing temperature. Considering the small number of experiments performed on sound absorption, which involve great experimental difficulties and large measurement errors, the results of measurements of $\alpha_{\text{exp}}(T)$ from Ref. 66, which were obtained later and are in good agreement with Ref. 65, are also indicated here.

As far as the relaxation time τ , appearing in Eq. (33b), is concerned, as already mentioned, estimates of it are quite provisional. The structural relaxation time τ_{η} is usually found with the help of a formula constructed by analogy to the relaxation time $\tau_{\eta'}$ of the shear viscosity:

$$\tau_{\eta''} = \eta'' / K'_{\text{tr}}, \quad (34)$$

where η'' is the bulk viscosity, whose numerical value is found from the condition

$$\alpha_m = (\omega^2 / 2\rho s^3) \eta'', \quad (35)$$

and

$$K'_{\text{tr}} = k_B T \rho N_A / M. \quad (36)$$

The formula (34) is usually based on the similarity of the physical processes responsible for momentum transfer in a

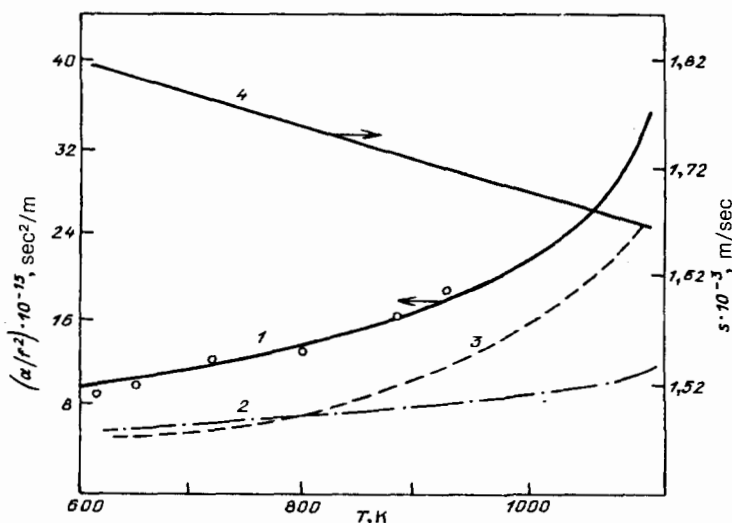


FIG. 2. Temperature dependences of the speed of sound (4) and sound absorption coefficient in liquid lead. 1—Experiment, 2—absorption due to heat conduction and viscosity, 3—relaxation absorption coefficient.

liquid between regions which are deformed differently and for restructuring of the short-range order under the action of elastic deformations. As justification of this estimate, it can be noted that for most low-viscosity melts it agrees in order of magnitude with the characteristic times of the autocorrelation function of the velocities of the particles, which is calculated with the help of the molecular-dynamics modeling (the numerical values of τ are presented in Table III). For purposes of estimation η'' was calculated from Eq. (35) from the known value of α_m or, if no experimental data on α_m were available, it was assumed that $\eta'' \approx \eta'$, which holds in the investigated melts quite well near the melting point T_m .

Substituting Eqs. (34)–(36) into Eq. (33b) we obtain that for the second term in parentheses estimation gives $K_{tr}/2\rho s^2 \ll 1$ and, therefore, if the formulas (34) and (35) are correct, then the bulk modulus K should likewise increase linearly with the temperature and in this case the relaxation contribution can be neglected.

On the other hand, for the instantaneous adiabatic bulk modulus within the statistical theory of liquids we can write⁶⁷

$$K \left(1 - \frac{k_B T \rho N_A \beta_T}{C_p M} \right) = \frac{k_B T N_A \rho}{M} + \frac{2\pi \rho^2 N_A^2}{9M^2} \left[\int_0^\infty \frac{d}{dr} \left(\frac{1}{r^2} \Phi'(r) \right) g(r) r^6 dr - 3 \frac{\partial}{\partial T} \int_0^\infty \Phi'(r) g(r) r^3 dr \right] \quad (37)$$

where the prime indicates differentiation with respect to r . By simple but cumbersome transformations we rewrite Eq. (37) in the form⁶⁸

$$K \left(1 - \frac{k_B T N_A \rho \beta_T}{C_p M} \right) = \frac{k_B T N_A \rho}{M} + \frac{4\pi \rho^2 N_A^2}{9M^2} \int_0^\infty \Phi(r) g(r) r^2 dr + \frac{2\pi \rho^2 N_A^2}{9M^2} \int_0^\infty \left[(6\Phi(r) - \Phi'(r)r) \frac{\partial g}{\partial r} - 3 \frac{k_B T N_A \rho}{C_p M} \Phi'(r) \frac{\partial g}{\partial T} \right] r^3 dr \equiv K_1 + K_2 + K_3, \quad (38)$$

where the fact that in metallic melts, as in liquified inert gases, for r greater than several interatomic distances $\Phi(r)$ decreases not more slowly than $\sim r^{-3}$ was taken into account. The second term can be expressed in terms of the potential energy U of the melt:

$$K_2 = 2U\rho N_A / M. \quad (39)$$

As far as the third term is concerned, in principle it can probably be calculated from the diffraction data obtained at different temperatures and pressures (it is easy to show that $\partial g / \partial r$ can be expressed easily in terms of $\partial g / \partial \tilde{V}$). The numerical values of K_2 in Eq. (39) can be estimated as the sum of heats which must be supplied to the melt in order for the melt to reach the boiling point and then evaporate. In Table

TABLE III. Comparison of the experimental values of the bulk moduli and their TCM with the values calculated from Eq. (39).

Element	$K_1 \cdot 10^{-10}$, Pa	$K_2 \cdot 10^{-10}$, Pa ¹⁾	$\frac{1}{K_2} \frac{dK_2}{dT} \cdot 10^4$, Pa	$\tau_{\eta''} \cdot 10^{12}$, sec ²⁾	$K_{exp} \cdot 10^{-10}$, Pa ³⁾	$\frac{1}{K_{exp}} \frac{dK_{exp}}{dT} \cdot 10^4$, K ⁻¹ 3)
Na	0,013	0,52	5,0	5,3	0,68	6,0
K	0,013	0,21	7,0	3,5	0,33	8,2
Cu	0,3	8,9	2,0	1,6	9,6	4,0
Ag	0,09	5,1	2,0	2,1	6,8	4,0
Mg	0,05	1,9	4,0	27	2,6	4,0
Ca	0,03	1,1	4,0	24	1,2	5,0
Zn	0,06	2,6	4	3,0	5,3	4,0
Cd	0,04	1,6	4	3,9	4,1	5,0
Hg	0,02	0,9	6	5,6	3,0	8,0
Al	0,07	6,1	2,0	4,8	5,3	2,0
Ga	0,05	5,5	2,0	3,7	5,0	3,0
In	0,02	3,4	2,0	2,1	3,8	2,0
Ti	0,03	2,2	2,0	30	3,1	4,0
Ge	0,08	6,0	1,0	9,0	4,0	4)
Si	0,12	7,6	0,65	6,4	3,9	4)
Sn	0,03	4,3	2,0	6,1	4,3	5,0
Pb	0,03	4,2	2,0	8,7	3,5	4,0
Sb	0,04	1,4	3,0	20	2,3	4)
Bi	0,02	1,8	3,0	69	3,0	3)
Ni	0,18	1,2	2,5	0,3	15,0	1
Co	0,18	11	2,5	0,2	12,4 [137]	1,1 [137]
Ar	0,0023	0,05	50	12 [69]	0,09 [135]	90 [135]
Xe	0,003	0,06	26	—	0,1 [136]	45 [136]

¹⁾The vaporization energies were taken from Refs. 69 and 138; the heat capacities were taken from Ref. 59.

²⁾The shear viscosities were taken from Ref. 59.

³⁾The references to the experimental investigations are indicated below in Table V.

⁴⁾The TCM changes with increasing temperature.

III the computed values of K_2 are compared with the experimental values K_{exp} . One can see that for close-packed melts from the first group the values do not differ by more than 10% (the heat capacities and heats of evaporation were taken from Refs. 59 and 69).

According to Eq. (39), the TCB is determined by the temperature dependence of the internal energy of the melt, i.e., the heat capacity, which, in agreement with experiment, is virtually independent of the temperature. The numerical values of TCB computed for close-packed metals from Eq. (39) agree in order of magnitude with the experimental values (the discrepancy is 20–40%).

The hard-sphere model gives good numerical agreement with the experimental values of the speed of sound.⁷⁰ However, the values of the TCB obtained within the hard-sphere model agree poorly. The model, for all practical purposes, does not convey the full diversity of the temperature dependence of s in semimetals and semiconductors, describing only the main feature of close-packed melts—the smallness of the free volume. Some improvement (but by no means complete) is obtained with the soft-sphere model, in which the temperature dependence of the radius of a sphere is introduced (see, for example, Ref. 71). The plasma models^{72,84} also ignore virtually completely the specific structure of the short-range order, giving only the correct order of magnitude of s . Thus, for these melts the relaxation contribution to K can apparently be neglected.

As far as the sound absorption coefficient is concerned, the temperature dependence of the contribution over and above the classical coefficient α_{cl} , calculated from the formula Eq. (33a), for melts of close-packed metals is approximated well by a function of the form $\alpha \sim T^3/s^3$ or by an exponential dependence of the type $\alpha \sim \exp(aT)$, where a is a constant. Obviously, if $aT \ll 1$, then both approximations give the same description of the experiment, since when the coefficient of proportionality is unknown the numerical term in the expansion of the exponential is masked by the linear increase of sound absorption with increasing temperature due to heat conduction.

The physical mechanisms of relaxation which are responsible for the excess sound absorption (as compared with the classical case) and giving the experimentally observed temperature dependence are still not entirely clear. On the one hand, melting of metals which in the solid state have the closest possible packing (twelfold coordination) is not accompanied by a significant change in short-range order (the coordination number ≈ 11), and the electric properties and measurements of the Hall constant indicate that the character of the conduction does not change, i.e., the type of interatomic bond remains the same, and this significantly limits the possible mechanisms of relaxation. On the other hand, since K_3 is 10–15% of the experimentally observed bulk modulus, this means that $\partial g/\partial \bar{V} \neq 0$ and (or) $\partial g/\partial T \neq 0$. Therefore, in the case of propagation of a longitudinal wave, the radial distribution function can change due to deformation and the change in temperature occurring in the wave. Since the translational displacement of atoms is controlled by processes of the diffusion type, this gives a phase shift between the deformation in the wave and the change in $g(r)$, i.e., structural relaxation appears.

In Ref. 74 it was suggested that in order to describe the contribution of a change in short-range order to sound ab-

sorption the packing ratio ξ_p be used as an additional independent thermodynamic variable and the excess sound absorption coefficient itself be calculated within the Mandel'shtam–Leontovich theory (see, for example, Ref. 32). The main deficiency of the theory of Ref. 74 is that it employs the free-volume model

$$\bar{v}_f = \frac{4}{3}\pi \left(\xi_p \frac{\bar{V}}{N_A} - a_{\text{at}} \right),$$

where a_{at} is the diameter of an atom, for deriving expressions for the free energy and its derivatives in the liquid metal. On the basis of this model, the potential energy of an atom, which depends on the short-range order, is written in the form $U = \gamma(\xi_p) N_A \bar{V}$, where $\gamma(\xi_p)$ is some function of ξ_p and completely ignores specific features of the metallic melts, such as the presence of free charge carriers and their screening action (which, essentially, is what leads to the specifically metallic pair interaction potential). The relaxation time of short-range order should correspond, in order of magnitude, to the residence lifetime and is estimated by A. I. Ansel'm for liquid mercury to be 10^{-13} sec. As far as the temperature dependence of α_r is concerned, the final formula in Ref. 74 (we do not present it because it is too complicated) contains parameters which are unknown in practice and it is difficult to say anything definite. Within this theory α_r should probably decrease with increasing T , since the residence lifetime of the atoms decreases.

Moreover, it is hardly useful to use the packing ratio as the relaxation variable, since the packing ratio is insensitive to details of the short-range order, as is evident from the fact that its values for different metallic melts are found to be very close to 0.45. This was one of the main justifications for using the hard-sphere model to describe the acoustic properties of metallic melts.

Two other approaches, employing similar ideas of structural relaxation in close-packed melts, were proposed practically simultaneously in Refs. 66 and 73. We note first that a quite large number of highly accurate diffraction experiments (see Ref. 1) have been performed in which it was observed that the average interatomic distances [position of the first maximum of $g(r)$] are virtually temperature independent in an entire series of fused metals and semiconductors whose specific volume increases with increasing temperature. This result is explained⁷⁵ within Ya. I. Frenkel's hole theory of the structure of liquids,⁷⁶ the main idea of which (ignoring the details, which are difficult to justify) is that as a result of intense translational (besides vibrational) motion of the structural units of the liquid, there arises a nonuniform spatial distribution of the so-called free volume, i.e., the volume not occupied by these structural units (for example, ions in metallic melts). Individual closed elements of free volume are called holes. Traditional calculations of the sound absorption coefficient within the hole theory of liquids³² are based on a postulated dependence of the probabilities of formation and vanishing of holes on the external conditions and they give, irrespective of the specific (more or less realistic) computational scheme, the result that the bulk η'' and shear η' viscosities are proportional and the proportionality coefficient is weakly temperature dependent. For this reason, the relaxation sound absorption coeffi-

cient should always decrease with increasing temperature, and this contradicts the experimental facts for close-packed metallic melts (Fig. 3).

For this reason, in Ref. 66 it was proposed that instead of calculating the probabilities of formation and vanishing of holes, the close-packed melt be regarded as a mixture of ions in two states (1 and 2): the first state corresponds to the case when there is no hole in the first coordination sphere, i.e., among the nearest neighbors of the ion, while in the second state the first coordination sphere contains one hole.

Using Furukawa's analysis⁷⁷ of the results on scattering of x-rays, Flinn, Jarzinski, and Litovitz⁶⁶ started from the assumption that in the absence of holes all liquid metals should have near the melting point short-range order with face-centered symmetry, which corresponds to $Z_c = 12$.

They attributed the fact that the real coordination number Z_r , found experimentally, is different from the ideal number Z_c to the presence of holes. This made it possible to calculate the number of holes in the first coordination sphere. The concentration of ions in the two states (1 and 2) was estimated, correspondingly, thus

$$c_2 = \frac{12 - Z_r}{Z_r}, \quad c_1 = 1 - c_2 = \frac{2Z_r - 12}{Z_r}, \quad (40)$$

and it was used as an additional thermodynamic variable. The transition of an ion from one state to the other is associated with transition through a definite potential barrier. This barrier is modeled by the deformation occurring in an elastic wave, which is what gives rise to relaxation. For this reason, the sound absorption coefficient is then calculated with the help of the two-structure model proposed by Hall⁷⁸ for describing acoustic properties of water and later elaborated by Herzfeld and Litovitz.⁷⁹ It was found that $\alpha_r \sim c_1 c_2$ and for this reason it is a strong function of the coordination number:

$$\alpha_r = \frac{c_1 c_2 \tilde{V} K^2}{2 \rho s^3 k_B T N_A} \left(\frac{\Delta \tilde{V}}{\tilde{V}} - \frac{\Delta H \cdot \beta_{T\infty}}{C_{P\infty}^M} \right)^2 \omega^2 \tau, \quad (41)$$

where $\Delta \tilde{V}$ and ΔH are the changes in the volumes and enthalpies per mole accompanying a transition of an ion from one state to the other; $\beta_{T\infty}$ and $C_{P\infty}^M$ are the instantaneous values

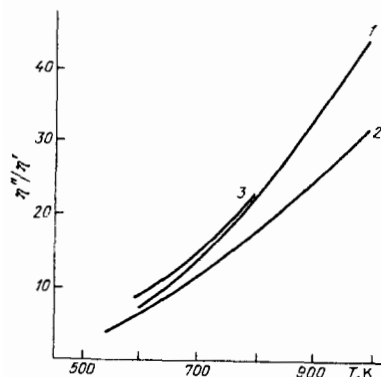


FIG. 3. Temperature dependences of the ratio of the volume η'' and shear η' viscosities for Pb (1), In (2), and Tl (3).

of the thermal expansion coefficient and the molar heat capacity at constant pressure; and, both concentrations are expressed in terms of the coordination number by the relations (39) and (40).

The mechanism of the interaction of an elastic wave at least with close-packed liquids, which liquid metals and semimetals are, is quite universal. For this reason, Z_c should probably be used as an adjustable parameter, since there is no basis for assuming that in all melted semimetals and semiconductors having in the solid state completely different types of short-range order and apparently several different interatomic potentials, the same value of Z_c (equal to 12) should be established after melting. Moreover, it is shown in a number of articles (see the bibliography in Ref. 3) that different radial dependences $g(r)$, in particular, dependences with a characteristic shoulder near the first peak, can be obtained by adjusting the pair potential.

It is easy to see that α_r as a function of the coordination number has a maximum at $Z_{\max} = 2Z_c/3$. For this reason, the behavior of $\alpha_r(T)$ is determined by the form of the function $Z_r(T)$. By adjusting Z_r it is possible to achieve good agreement with experiment with respect to both the temperature dependences of α_r and the absolute magnitude. However, in using the theory it is necessary to take into account the fact that the computational results depend very strongly on Z_r , whose value is determined with large error from direct experiments. Thus, for Pb $Z_r = 11.4$ gives good agreement with the measured value of α_r , and $Z_r = 11.2$ or $Z_r = 11.6$ gives disagreement with respect to both the absolute magnitude of α_r and its temperature dependence. Similar results are also obtained for Bi.

We note in passing that for close-packed metals $\alpha_r(T)$ is a monotonically increasing function. This follows from Eq. (41), if $Z_r > Z_{\max}$, since the coordination number decreases with increasing temperature. In these metals the assumption $Z_c \approx 12$ probably is justified, since $Z_{\max} = 8$ and near the melting point $Z_r \approx 11$. In liquid bismuth (see below, Fig. 6), however, these arguments are not valid, since the coordination number is much smaller than eight in this case,⁸⁰ and therefore on the section where α increases monotonically $Z_c < 12$, which, considering the character of the interatomic interaction in the crystalline state, is entirely reasonable. The described computational scheme can also be used for calculating α_r within the cluster model of a liquid, which, in the last few years, has been employed quite widely for describing different properties of liquids (see Ref. 1). Here, two states of the ions can also be separated: in the first state an ion is present in the cluster and in the second state an ion is present on the boundaries of the clusters (or between clusters). We return to this question below when we discuss the acoustical properties of melts of semimetals and semiconductors.

In Ref. 73 the packing ratio ξ_f of the free volume was chosen as the additional independent thermodynamic variable which takes into account the presence of holes. It was introduced into the calculation by the definition

$$(4/3)\pi(\bar{r}^2)^{3/2}\xi_f = \bar{v}, \quad (42)$$

where $(\bar{r}^2)^{1/2}$ is the rms interatomic distance and \bar{v} is the specific volume per ion. It is easy to express \bar{r}^2 in terms of the radial distribution function $g(r)$, since the latter function,

being a binary correlation function, is related to the probability of finding a particle at a distance ranging from r to $r + dr$ from some other particle:⁶⁸

$$\bar{r}^2 = \frac{1}{\bar{V}} \int r^2 (g(r) - 1) d\bar{V}. \quad (43)$$

Introducing $r = \bar{r} + \Delta r$ and $\bar{v} = \bar{v}_0 + \Delta \bar{v}$, where \bar{r} is the average interatomic distance corresponding to the first maximum in $g(r)$, $\bar{v}_0 = (4/3)\pi\bar{r}^3$, Δr are random deviations from the average values in the interatomic distances, and $\Delta \bar{v}$ is the free volume per ion, and assuming that $\Delta r \ll \bar{r}$, we can rewrite Eq. (42) in the form

$$\frac{(\Delta r)^2}{\bar{r}^2} \approx \frac{\Delta \bar{v}}{\bar{v}_0}.$$

In this approach sound absorption is due to relaxation arising as a result of the redistribution of free volume under the action of the elastic wave. A relation between ξ_r and the free energy of the melt can be found on the basis of the pseudopotential theory,⁸¹ applied to metallic melts under quite general assumptions about the form of the local pseudopotential. The internal energy of the melt can be written as⁸¹

$$U = U_0(\bar{V}) + \frac{1}{2\pi^2} \int_0^\infty \int_0^\infty U_n(Q) + U_k(Q)(g(r) - 1) \frac{\sin Qr}{Qr} r^2 Q^2 dr dQ, \quad (44)$$

where $U_0(\bar{V})$ includes all terms in the expansion of the internal energy which depend on the volume of the system and the second term takes into account the energy that is sensitive to the structure of the short-range order; $U_{\text{dir}}(Q)$ and $U_{\text{indir}}(Q)$ are the Fourier transforms of the pair potentials of the direct and indirect (via the conduction electrons) interactions.

The integral over the wave number Q in Eq. (44) is estimated on the basis of the fact that $U_{\text{dir}}(Q)$ and $U_{\text{indir}}(Q)$ are proportional to $\varepsilon(Q)$ [$\varepsilon(Q)$ is the Fourier transform of the dielectric permittivity of the electron gas], and $\varepsilon(Q)$ has a logarithmic singularity at $Q = 2Q_F$ (Q_F is the Fermi wave number).

In Ref. 73 calculations were performed for a pseudopotential in the point-ion model taking into account repulsion of the internal shells. As a result we have

$$\alpha_r \approx \frac{0.1\omega^2\tau}{2\rho s^3} \frac{z^2 q_e^2}{\varepsilon^2(2Q_F)\bar{v}^{4/3}} \xi_r^{-2/3}, \quad (45)$$

where z is the valence and q_e is the electron charge. This gives the correct order of magnitude, if it is assumed that $\tau \approx 10^{-12}$ sec. The temperature dependence of α_r can be estimated taking into account the fact that within the Mandel'shtam-Leontovich relaxation theory³² $\tau \sim \partial^2 U / \partial \xi_r^2$. Hence⁷³

$$\alpha_r \sim T^3/s^3. \quad (46)$$

In Fig. 4 the computed temperature dependences $\alpha_r(T)$ are compared with the experimentally found dependences (dots) for Pb, In, Bi, and Tl. The proportionality coefficient in Eq. (46) was found by comparing the theoretical and experimental values at a given temperature. As far as the relaxational contribution to the sound speed is concerned, in virtually all theories considered above $\Delta s_r \sim 1/T$, which should lead, from Eq. (33b), to a positive TCB. If, however, the previous estimate 10^{-12} sec is used for τ , then for real values of α_r the second term in Eq. (33b) can be neglected and therefore the temperature dependences of K_{exp} in close-packed metals from the first group are determined only by the instantaneous values of the bulk modulus, and this leads to linear temperature dependences $K_{\text{exp}}(T)$.

1.2.2. Acoustic properties of group-2 metals

The experimental observation of the characteristics of the acoustic properties of metallic melts from the second

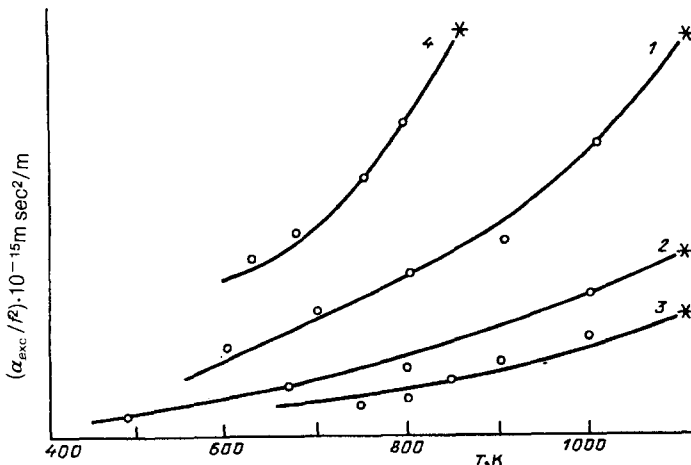


FIG. 4. Comparison of the experimental results with the function $\alpha_r \sim T^3/s^3$ for Pb (1), In (2), Bi (3), and Tl (4). The asterisk marks points where both dependences coincide.

group (Zn, Cd, Hg) reduces to the following. In these melts the TCB is substantially nonlinear,⁸² and $\alpha(T)$ exhibits a nonmonotonic temperature dependence.⁶⁵ This is illustrated in Fig. 5 for the example of Zn.

In addition, the acoustic properties of these melts are several times more sensitive to external pressure than for other metallic melts (for example, for melts belonging to the first group $s^{-1}ds/dP \approx 0.6 \cdot 10^{-5} \text{ bar}^{-1}$, while for mercury $s^{-1}ds/dP \approx 1.5 \cdot 10^{-5} \text{ bar}^{-1}$,^{83,84} this last result agrees well with the values of $\partial g/\partial \tilde{V}$ estimated from the calculations of $(K_{\text{exp}} - K_2)/K_{\text{exp}}$ presented in Table III. The latter quantity is 10–20% for group-1 close-packed metals and 100–200% for Zn, Cd, and Hg.

The excess sound absorption coefficient in Zn and Cd has a diffuse maximum. This agrees well with x-ray measurements in a wide temperature range,⁵⁵ which show that in these melts, even though the character of the metallic bond does not change, the coordination number at first increases and then starts to decrease at 100–200° above the melting point. It is easy to see that within any model of the melt an increase in the coordination number with the bond type remaining unchanged is accompanied by an increase in the bulk modulus. This increase, superposed on the overall drop in the bulk modulus due to intensification of thermal motion accompanying heating, decreases the TCB in group-2 metals.

The increase in the coordination number near the melting point T_m in these metals is probably connected with the fact that in the solid state they have a complicated structure of short-range order (8 + 6) and the change in short-range order is not completed in them at T_m . Analysis of the change in the bulk modulus of these metals on melting gives similar results (see below).

We also note that the significantly lower TCB than in other group-1 metals has also been observed in In (see Table III), in which conversion of the short-range-order structure from a body-centered cubic lattice (8 + 6) in the solid state to the closest packed structure in the melt occurs also. X-ray diffraction experiments also show that the coordination number in indium does not reach immediately values characteristic for the closest packing (11, 8), but rather increases

smoothly after melting.

In In, however, the TCB is practically constant (except for the case of large overheatings), and α_m is a monotonic function of the temperature.^{63,65} The reasons why bivalent metals are more sensitive to changes in the coordination number (and external pressure) must be sought in the presence of two valence electrons, since, as is well known (see, for example, Ref. 85), in the solid state their valence band overlaps with the band lying above it, and on melting the electric properties of In and the density of mobile charge carriers do not change drastically. Since the radii of both coordination spheres of the corresponding crystals fall into the region of the first maximum of the radial distribution function of fused Zn, Cd, and Hg, it can be conjectured that there are present in the melt two close preferred interatomic spacings and hence two values of the overlappings of the bands. This makes it possible to employ two-structure models, similar to the two-state models considered above, for calculating α_m .^{66,86} Both studies are ideologically close to the model presented above; they differ by the methods employed for finding the values of the adjustable parameters. In the first approach (Ref. 66) $\alpha_r \sim c_1 c_2$ and in the second approach (Ref. 86) $\alpha_r \sim c_1 c_2^2$, where c_1 and c_2 are the concentrations of each structure and $c_1 + c_2 = 1$. The difference is connected with the formula used to calculate the contribution of translational motion to the bulk modulus of the melt and, as a consequence, different values are employed for the relaxation time. In Ref. 66 K'_{tr} is calculated from Eq. (36) and in Ref. 86 $K'_{tr} = c_2 K'_{tr}$. If c_1 and c_2 are functions of the temperature, then in accordance with experiment α_r has a maximum at $c_1 = 0.5$ in the first case and $c_1 = 0.3$ in the second case. For large overheatings the differences between the structures vanish due to intensified thermal motion, and the temperature dependence $\alpha_m(T)$ is determined by processes which are characteristic of close-packed metals.

1.2.3. Acoustic properties of melts of semimetals and elemental semiconductors

The clearest relation between the acoustic characteristics of close-packed monatomic liquids and the organization of short-range order is observed in melts of elements belong-

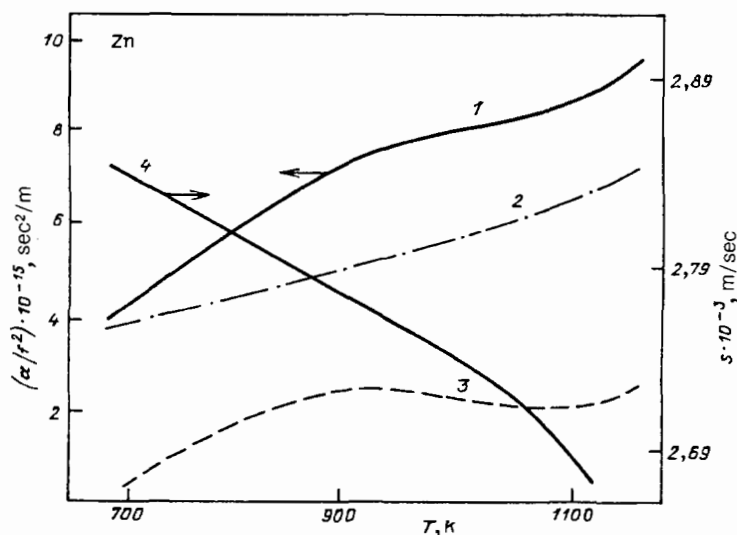


FIG. 5. Same as Fig. 2 but for liquid zinc.

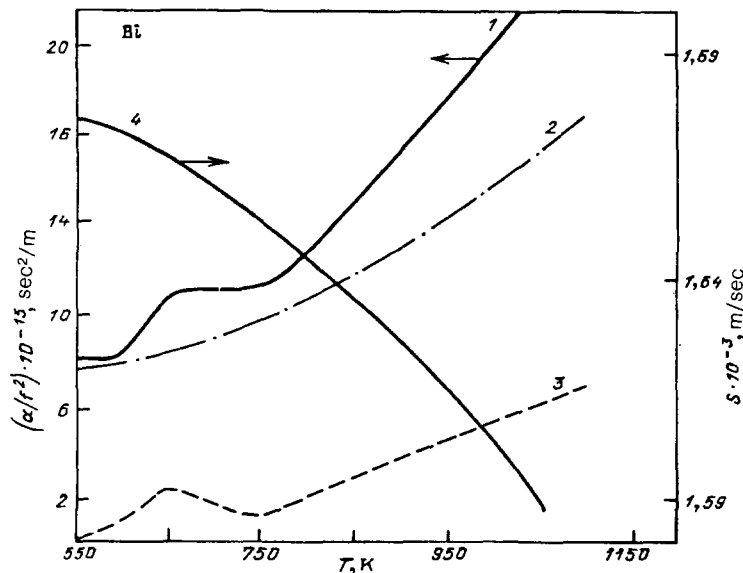


FIG. 6. Same as Fig. 2 but for liquid bismuth.

ing to the third group—in semimetals and semiconductors. As has already been mentioned, experiments have established reliably that for these melts the first peak in the scattering intensity as a function of the angle is accompanied by a secondary peak. The coordinate of the secondary peak often corresponds to the distance to the nearest neighbors which form a homopolar bond in the solid state.^{3,55}

From the standpoint of acoustics the temperature dependences $s(T)$ and $\alpha(T)$ in group-3 melts differ significantly from the first and second groups.

In fused tin and gallium,^{63,64,87,88} as in group I metals, the bulk modulus is observed to decrease with increasing temperature, but significantly above the melting point ($\sim 275^\circ\text{C}$ for gallium and $\sim 570^\circ\text{C}$ for tin) the TCB changes significantly.

Similar features are also observed in the temperature dependences $\alpha(T)$ for tin, though these temperatures are appreciably lower than the ones at which the secondary peak in the $g(r)$ curve vanishes.³ The changes in the TCB amount to 10–15% and some authors have not been able to record them at all (see the bibliography in Refs. 59 and 84). Recent

measurements performed by S. G. Kim have revealed a peak in the sound absorption coefficient of fused gallium right next to the melting point,¹³³ though earlier measurements performed by Hunter and Hovan^{133,134} did not show this feature. The results obtained in this temperature range^{88,133,134} are also distinguished based on the measured absolute values of α . At temperatures high above the melting point the sound absorption coefficient increases monotonically approximately as T^3/s^3 with increasing temperature.

As the fraction of covalent bonds in the solid state increases, the transition into the liquid state results in more complicated temperature dependences $s(T)$ and $\alpha(T)$. They are presented in Fig. 6 for Bi,⁶³ in Fig. 7 for Sb,^{63,97,98} in Fig. 8 for Ge,^{91,93} in Fig. 9 for Si,^{94–96} and in Fig. 10 for Te.^{63,97,98}

As one can see from the plots of $s(T)$, in all melts near the melting point the bulk modulus does not decrease with increasing temperature, as in typical metallic melts, but rather it either remains practically constant (for Bi; see also Refs. 59 and 84) or it increases with the temperature (for Ge, Sb, Si, Te). Only at temperatures significantly above the melting point (Bi, Ge) is it possible to observe a transition to

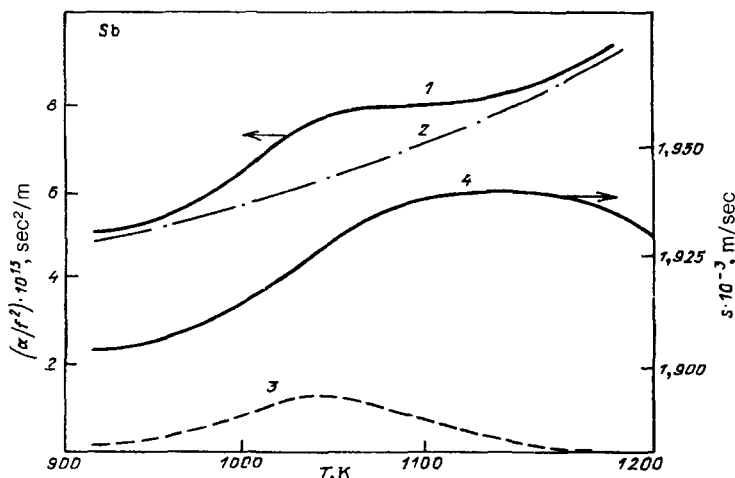


FIG. 7. Same as Fig. 2 but for liquid antimony.

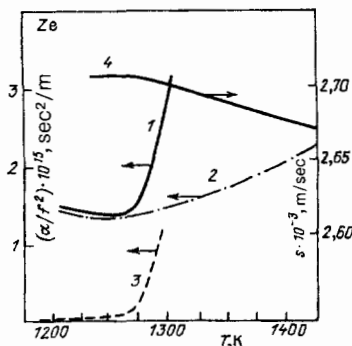


FIG. 8. Same as Fig. 2 but for liquid germanium.

a bulk modulus that decreases linearly with increasing temperature or to a different TCB (Sb, Te).

The sound speed as a function of the external pressure behaves near T_m differently from the case of normal metals. Such experiments up to pressures $P = 12$ kbar have been performed for liquid bismuth^{83,84,89} and have revealed a significant difference in $s(P)$ near and high above the melting point.

The temperature dependence $\alpha_m(T)$ in fused semimetals and semiconductors, in contradistinction to group I metals, has near T_m peaks of different height and a transition to the temperature dependence $\alpha_m \sim T^3/s^3$ can be observed only far above the melting point (Bi, Te).

As expected, all features in $s(T)$ and $\alpha_m(T)$ are most clearly observed in tellurium melt, where melting and heating make it possible to realize semiconductor-semiconductor—metal transitions.

It is natural to associate the features in the acoustic characteristics of fused semimetals and semiconductors to the characteristic features of the organization of short-range order in them, since the latter features are recorded reliably in diffraction experiments. Thus, it has been established in Bi (Ref. 80) that in the temperature range 20–30 K above the melting point the coordination number Z_r increases from 7.2 to 8.1 and then decreases monotonically. Similar changes in the coordination number are observed in diffraction experiments in Sb, Ge, and Si. In the case of tellurium, the temperature changes occurring in the radial distribution function are interpreted⁹⁹ as resulting from preservation of chains of tellurium atoms in the melt immediately after melting. Heating decreases the length of the chains, but the directed covalent bonds remain even with quite large overheating;

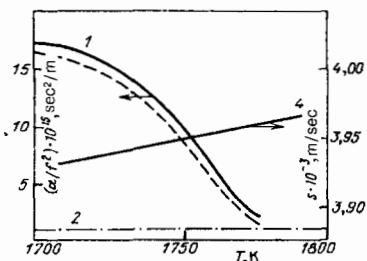


FIG. 9. Same as Fig. 2 but for liquid silicon.

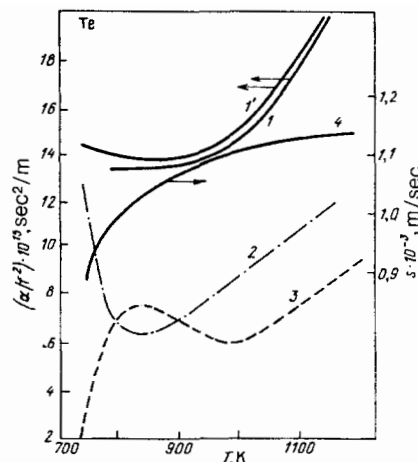


FIG. 10. Same as Fig. 2 but for liquid tellurium. 1'—experimental curve obtained in Ref. 98.

ings; this is also indicated by the fact that the position of the first peak in $g(r)$ remains virtually unchanged as a function of the temperature and the second and third peaks in $g(r)$ are well resolved.¹⁰⁰ At higher temperatures (up to 400 K above T_m) the second and third peaks in $g(r)$ vanish, and the coordination number increases up to 6.

We underscore, however, the fact that the secondary peak in $g(r)$, which has served as a basis for separating the third group of melts and is usually interpreted as being a consequence of the preservation of covalent bonds, is observed at temperatures appreciably above the range where anomalies are present in the acoustic characteristics. In this connection we note that anomalies in the temperature dependences of different physical properties of group III melts have been observed by many authors (see the reviews in Refs. 55, 59, and 101). Thus, measurements of the electrical conductivity σ have shown that after melting σ in Bi, Sb, Ge, and Si reaches values close to the typical values for polyvalent metals (for example, Pb), and this enabled A. R. Regel¹⁰¹ to assert that melting in these metals results in semimetal-metal and semiconductor-metal transitions, respectively, for Bi, Sb and Si, Ge.

Accurate measurements of the electrical conductivity and the Hall constant have revealed that in a number of cases the transition is not completed at melting, but rather it continues also in the liquid state. Thus, in the case of Ge at temperatures of 50–60° above the melting point σ deviates from a function which decreases linearly with increasing temperature and the Hall constant passes through a minimum.⁵⁹

However, no sharp anomalies in the electrical properties of Bi and Sb have been observed above the melting point, though near melting the Hall constant of these metals is somewhat different from the values predicted by the free-electron model under the condition that all valence electrons are collectivized.

The activation energy of viscous flow in all liquid polymers (Bi and Sb) and semiconductors (Ge and Si) near T_m changes as a function of temperature more slowly than at higher temperatures, and in some elements it passes through a minimum.¹⁰¹

In tellurium intense growth of the electrical conductivity and viscosity changes extend over several hundreds of degrees, and the Hall constant decreases, remaining ~ 3 times higher than in the free-valence-electron model.⁵⁹

Thus in all structure-sensitive physical properties of melts of semimetals and semiconductors (except Te) anomalies are observed mainly at temperatures slightly above the melting point, when no drastic changes are observed in the secondary peak in the intensity of x-ray scattering, but rather changes, reflecting small changes in the coordination number, are observed in the main peak itself.

One would think that the anomalies in the acoustic characteristics reflect directly a continuing increase of the free-carrier density near the melting point. However, replacing the covalent bonds by metallic bonds does not increase the bulk modulus, but rather it decreases the bulk modulus substantially, and this can be seen clearly in Table V for the example of germanium and silicon. In these metals, in spite of the fact that the volume decreases substantially on melting, the bulk modulus decreases strongly, and this can be correlated to the fact that the interatomic bonds become metallic.

Another possible explanation, based on the fact that on melting a large relaxation compressibility arises in the semiconductors, does not work because the experimentally observed sound absorption coefficients are very different, even though their bulk moduli change by approximately the same amount on melting. However, the general relaxation relations (33) show that this situation can occur only if the relaxation times in both melts are substantially different, and there is no physical basis for this (these melts have close viscosities and specific volumes, which determine the translational relaxation time).

Anomalies in the behavior of the physical properties near the melting point of liquid metallizing semimetals and semiconductors are often regarded as a manifestation of their microscopically nonuniform cluster structure.

Hall's two-structure approach,⁷⁸ mentioned above, was proposed as a relaxation mechanism already in the first papers in which acoustic anomalies were observed in liquid semimetals and semiconductors.^{63,64,97} Within the two-structure model, quasicrystalline structure is assigned to the liquid. According to this structure, the liquid consists of a mixture of two structures: one corresponds to the solid state and the other corresponds to a more close-packed state. The appearance of a close-packed structure is what determines the decrease in the volume on melting. Atoms can make a transition from one structure into another, but this transition requires overcoming some potential barrier. The relaxation process arises as a consequence of the modulation of the probabilities of a transition of atoms from one structure into another by the elastic wave and therefore as a consequence of changes in the concentration of both structures.

One version of the two-structure model is the cluster model proposed for a liquid quite a long time ago (see the bibliography in Refs. 3 and 102) and recently further elaborated in the theory of melting and premelting.^{103,104} A. R. Regel' and V. M. Glazov explained, with the help of the cluster model, anomalies in the temperature dependences of the viscosity near the melting points in melts of semimetals and semiconductors.¹⁰² V. R. Regel', V. M. Glazov *et al.* employed in a number of studies (see the review in Ref. 105)

cluster representations for qualitative interpretation of the above-noted features in the experimental temperature dependences of the speed of sound in melts of semiconductors. In these papers the different temperature behavior of the physical properties in liquid semimetals and semiconductors was attributed to the different kinetics of cluster breakup. However, as a comparison of the bulk moduli of semimetals and semiconductors, which metallize on melting, in the solid and liquid states (see Table V below) shows, the breakup of solid-like clusters should by no means result in an increase of the bulk modulus, which is required for explaining the experimental results.

It should also be noted that J. Ziman's general considerations¹⁰⁶ concerning the fact that the role of a large number of "special" atoms located on the surface of clusters is neglected are not resolved within the traditional cluster analysis.

Cluster representations also contradict Turner's thermodynamic estimates (see Ref. 107). He obtained for the structure factor $S(0)$ of a binary alloy in the small-angle limit

$$S(0) = N_{cl}(c_A - c_{cl})(c_M - c_{cl}),$$

where N_{cl} is the number of atoms in a cluster, C_A is the total concentration of atoms of, for example, type A , c_{cl} is the atomic concentration of A atoms in a cluster, and c_M is the concentration in the matrix in which the clusters float. Numerical estimates give for N_{cl} values of 1–2, which, of course, is physically meaningless.

It is also difficult to reconcile the idea of clusters as crystal-like formations with the results of diffraction experiments which show that the temperature dependence of the coordinate of the first peak is very weak (or absent altogether), i.e., the microscopic thermal expansion coefficient for different melts, including bismuth and germanium,^{55,56} is very small (zero), though the presence of regions with crystalline order would also require the organization of crystalline thermal motion with values of β_T typical for the corresponding crystals.

As far as the secondary peak is concerned, there exist a number of methods (see the bibliography of Ref. 3) for obtaining it, for example, with the help of a specially chosen pair interaction potential.¹⁰⁸

In addition, molecular-dynamics modeling of melts, in particular, recent calculations for liquid Si (Ref. 90) and GaAs (Ref. 107), does not reveal any clusters. However, modeling has shown for Si that $\approx 30\%$ of the atoms in a coordination sphere are associated with the central atom, while for GaAs up to 50% of the atoms are associated with the central atom. Moreover, in gallium arsenide, if the probability of strong coupling between atoms of the same type is 27%, then the probability of coupling between groups of three atoms drops to 6%.

These bonds could possibly be present in the form of short-time localization of valence electrons in the bound state between pairs or groups of neighboring atoms, for example, in the process of resonance hybridization,⁵⁵ as considered by Pauling.¹⁰⁹

A significant difference between the covalent and metallic bonds is that covalent bonds have a finite lifetime τ_{life} , since they are broken by the thermal diffusive motion. This was also demonstrated by molecular-dynamics modeling in

Ge and GaSb. Considering the fact that a finite time τ_g is required in order to establish a covalent (ionic) bond and τ_{life} decreases with increasing temperature, since thermal motion intensifies, it is understandable, without the help of the cluster model, why in melts such as Ge, Si, Bi, and Sb, covalent bonds are broken and metallic bonds are established (if the density permits this to happen) as the temperature increases.

This approach enables a natural explanation of the experimental fact that in the amorphous state (static disorder) in Ge and Si the main type of bond is the covalent bond, while in the liquid state (dynamical disorder) the main type of bond is metallic. If, however, the material in the crystalline state has a chain-like structure, then the weakest bonds are the interchain bonds, and melting occurs as a result of breaking of these bonds. The melt contains a large number of chains, which are not broken by the thermal motion. As a result, chains are the structural units which participate in the translational motion. Such a system has a high viscosity, and therefore the residence lifetime of the structural units is long. For this reason, the covalent bonds are mainly preserved, and melting occurs by semiconductor-semiconductor (selenium) and dielectric—dielectric (sulfur) type mechanism. The intermediate case is apparently realized in tellurium, when the energy of bonds between atoms in a chain is comparable to the interchain bond energy. As a result, on melting there appears a metallic type interatomic interaction together with weak self-diffusion and a high content of covalent bonds. The latter bonds quickly break with increasing temperature, since the viscosity decreases rapidly.

Thus atoms in Ge, Si, Bi, and Sb probably occupy two states, while in Te they occupy three states. The first case is characterized by a purely metallic type of interatomic bond, while the second case is characterized by a mixed covalent-metallic bond. Atoms comprising chains with a covalent bond are found in the third state. Deformations in an elastic wave displace the dynamical equilibrium between concentrations of atoms c_i in different states, and this gives rise to the appearance of relaxation effects, which are superposed on the above-considered universal mechanism of relaxation characteristic of all close-packed liquids due to modulation of the free volume by the elastic wave. Since in metallizing semimetals and semiconductors (except for tellurium) the concentration of atoms with a covalent bond is low, an appropriate model for theoretical description of the relaxation process could be the weak-solution model, considered in Ref. 1, in which the solvent is the medium with a metallic bond and the solute are atoms with a covalent bond. Using calculations of the sound absorption coefficient, associated with the modulation of the probabilities, given in Ref. 1, of the creation of thermal fluctuational defects, we obtain for α_r

$$\alpha_r \approx \left(\frac{\beta_T k_B T \ln c_{\text{cov}}}{\rho C_V} + \frac{\Lambda_{\text{liq}}}{K} \right)^2 \frac{c_{\text{cov}} K^2 N_A \omega^2 \tau_{\text{life}}}{2s^3 k_B T M}, \quad (47)$$

where c_{cov} is the concentration of covalently bonded atoms, C_V is the heat capacity at constant volume, M is the gram-atomic weight, N_A is Avogadro's number, Λ_{liq} is the deformation potential, characterizing the modulation of the potential barrier to the breaking of a covalent bond by the

deformation in the wave. As noted in Ref. 1, if in order to remove an atom creation of a free volume Ω is required, then $\Lambda_{\text{liq}} \equiv K\Omega$. The first term in parentheses takes into account the contribution to the sound absorption of the change in temperature in the elastic wave.

It is easy to see that Eq. (47) describes qualitatively correctly all the basic features of α_m , observed experimentally in melts of semimetals and semiconductors. Indeed, in accordance with Eq. (47) α_r has a maximum if

$$c_{\text{max}} = \exp \left[- \left(2 + \frac{\Lambda_{\text{liq}} C_V}{K \beta_T k_B T} \right) \right]. \quad (48)$$

The height of the maximum is

$$\alpha_{r,\text{max}} = 2c_{\text{max}} \beta_T^2 k_B T K^2 N_A \omega^2 \tau_{\text{life}} / C_V^2 M s^3. \quad (49)$$

In order to estimate the deformation potential we can set $\Lambda_{\text{liq}} \approx K(b r_1^3)$, where r_1 is the radius of the first coordination sphere and b is a numerical coefficient of order unity. Then we obtain $c_{\text{max}} = 10^{-2}$, and $\alpha_{r,\text{max}}/f^2 = 10^{14} - 10^{15} \text{ sec}^2/\text{m}$, if $\tau_{\text{life}} \approx 10^{-11} - 10^{-12} \text{ sec}$, which agrees in order of magnitude with the experimental results. Since from general considerations it is obvious that the concentration of covalent bonds should decrease with increasing temperature, the condition for observing a maximum in $\alpha_r(T)$ is $c_{\text{cov}} > c_{\text{max}}$, and the condition for $\alpha_r(T)$ to decrease monotonically is $c_{\text{cov}} < c_{\text{max}}$. The first case is realized in fused bismuth and antimony, and the second case is realized in liquid germanium.

As one can see from Eqs. (33a) and (33b), if α_r decreases, then Δs should also decrease, and hence the measured sound speed should increase. Precisely such behavior is observed in silicon. For this reason, the absolute value and temperature dependence for τ_{life} can be obtained with the help of Eq. (33b) and experimental data for s and α_m in the temperature interval $T_m - T_m + 100$. In Fig. 11 it was assumed that at 1800 K, when α_m dropped by an order of magnitude and no longer changed with increasing temperature, the effect of the relaxation mechanism considered is small and the universal relaxation mechanism associated with modulation of the free volume (see above) becomes determining. The results of such analysis, which are presented in Fig. 11, show that the estimate $\tau_{\text{life}} \approx 10^{-11} \text{ sec}$ is self-consistent. We note that the structural relaxation time τ_η , calculated from Eqs. (34) and (36), under the assumption that it is equal to the relaxation time of the shear viscosity

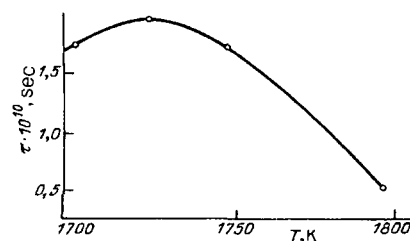


FIG. 11. Temperature dependence of the covalent bond lifetime in liquid silicon.

($\eta'' \approx \eta'$), gives the estimate 10^{-12} sec, i.e., $\tau_{\eta'} \gg \tau_{\text{life}}$. This result is entirely justified physically, since the shear viscosity is determined by the motion of atoms with a metallic type bond, which comprise $\sim 99\%$ of all atoms in the melt, while the energy of the metallic bond, as a comparison of the bulk moduli in the solid and liquid states in Ge, Si, Bi, Sb shows, is less than that of the covalent bond. Calculating Δs for liquid germanium using the same estimate for τ_{life} shows that the change in the sound speed due to the relaxation process under consideration is small and cannot explain the experimental temperature dependences $s(T)$.

Estimates of Δs for liquid Bi and Sb lead to a similar conclusion. Moreover, in accordance with Eq. (33), the situation cannot be saved even by adjusting the numerical value of τ_{life} , since as α_r increases, Δs increases and therefore s decreases, and vice versa. As a result of this, relaxation theories cannot be used at all to explain at the same time the maxima of Δs and α_m , provided that the relaxation mechanism does not presuppose an effective increase of the relaxation time with increasing temperature. This situation can be interpreted as being a consequence of the fact that the temperature dependence of the sound speed in these melts is determined not by a relaxation process, but rather by a change in the instantaneous bulk modulus due to the change in the short-range order on heating near the melting point; this is manifested in the above-noted change in the first coordination number, which, as the temperature increases, at first increases and then decreases [see Eq. (38)]. This interpretation is also supported by the fact that the temperatures of the maxima of $\Delta(T)$ and $\alpha_m(T)$ are not the same.

Significantly above the melting point the concentration of covalently bonded atoms decreases; τ_{life} also decreases, which gives rise to a significant decrease in α_m according to this mechanism of interaction. The above-considered relaxation mechanism, associated with modulation of the free volume by the elastic wave in close-packed liquids, increases at the same time with increasing temperature. As a result the temperature dependence $\alpha_m(T)$ is described by the function T^3/s^3 .

This picture is seen most clearly in liquid bismuth, which has been studied experimentally right up to temperatures above $2T_m$ (see Fig. 6).

The ideas presented above should explain the temperature dependence of the acoustic properties of binary systems, demonstrating semimetal and semiconductor properties in the liquid state, which were studied in a number of articles by V. M. Glazov and S. G. Kim,¹⁰⁵ who attributed the observed anomalies to the cluster (microcrystalline) structure.

1.2.4. Acoustic properties of melts of monatomic dielectrics

The close correlation between the temperature dependence of the acoustic properties and changes in the organization of short-range order is also observed in melts with a large free volume, in which covalent bonds are the predominant interatomic interaction forces. Among the monatomic liquids, we consider as examples sulfur and selenium, in which heating above the melting point is accompanied by strong, similar changes in short-range order.

The chain-like structure of the crystals of these substances—strong interatomic interaction in a chain and weak interchain interaction—indicates that the atomic potentials

are anisotropic, and this undoubtedly should be manifested in the organization of the short-range order in the corresponding melts.

It is well known⁹⁹ that immediately after melting elements characteristic for the crystalline structure are observed in the structure of short-range order of selenium: Se_8 rings—comprising a monoclinic modification and spiral chains—the structural units of hexagonal selenium. When the temperature increases up to 573 K, the chains break and the concentration of Se_8 rings increases. When the temperature increases further to 703 K, the rings break and short chains form.

Heating liquid sulfur also significantly changes the short-range order: from weakly bound S_8 rings to low-molecular formations S_2 and S_3 and then long molecular chains. These structural transformations are accompanied by such a strong change in the character of the translational motion that the viscosity of the melt has a maximum which is five orders of magnitude greater than the value near the melting point. The temperature dependences, constructed from the data of Refs. 110 and 111, of the acoustic properties of Se are presented in Fig. 12. We note in passing that the temperature dependences presented for α and s for liquid selenium agree well with later results obtained in Ref. 112 for both the character and value and with the results of Ref. 113 for only the character of the temperature dependences. The acoustic properties of liquid sulfur were investigated in Refs. 110 and 111 and have a similar temperature dependence.

The complicated temperature dependence $\alpha(T)$ reflects the transformation of the short-range order as a function of temperature in both liquid selenium and sulfur melt. We shall discuss in greater detail the results of acoustical experiments in selenium in order to reveal in their acoustical characteristics possible channels for manifestation of short-range order in liquids.

At low temperatures (near the melting point) the dynamical viscosity of liquid selenium is high due to the presence of spiral chains (according to the reference data from Ref. 59 for $T = 500$ K $\eta'/\rho \approx 10^{-4} \text{ m}^2 \cdot \text{sec}^{-1}$). If the sound absorption coefficient $\alpha_{\eta'}$ associated with the viscosity η' is estimated and compared with the experimental values, it is easily seen that the theoretical values are several times greater than the experimental values, i.e., in contradistinction to metallic and metallizing melts the relaxation of the viscosity and $\alpha_{\eta'}$ should conform here to the formula³²

$$\alpha_{\eta'} = (K_{\eta'}/2\rho s^3) \omega^2 \tau_{\eta'} / (1 + \omega^2 \tau_{\eta'}^2), \quad (50)$$

where $K_{\eta'}$ is the contribution of relaxation of the shear viscosity to the bulk modulus. This opens up the possibility of checking the scheme presented above for the relaxation of the shear viscosity. The condition under which $\alpha_{\eta'}$ has a maximum makes it possible to calculate $\tau_{\eta'}$ and, if $\eta'(\omega = 0)$ is known, then $K_{\eta'}$ can also be calculated. The latter value can be compared with the value calculated from Eq. (36). Next, knowing $\eta'(\omega = 0)$ and $K_{\eta'}$ it is possible to calculate $\alpha_{\eta'}$. Numerical estimates using data on the shear viscosity from Ref. 59 show that the formula (50) describes not only qualitatively, but also quantitatively the behavior of α in Se at 60 MHz.

The quantity $K_{\eta'}$ is estimated to be 2% of the instantaneous bulk modulus. This, on the one hand, agrees well with

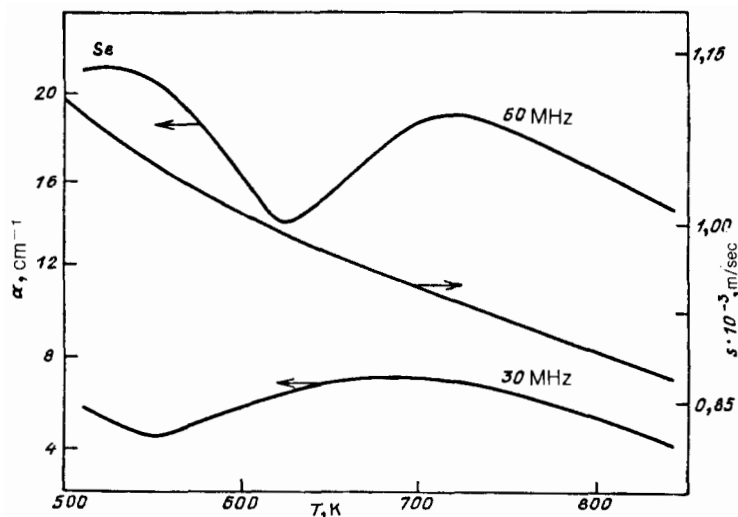


FIG. 12. Same as in Fig. 2 but for liquid selenium.

the theoretical value and, on the other, explains the absence of any anomalies in the temperature dependence of the speed of sound. It is easy to see that at 30 MHz the temperature of the maximum of $\alpha(T)$ shifts toward lower temperatures and ends up near the melting point, where it is difficult to perform reliable measurements.

As the temperature increases, the chains become shorter, the viscosity drops, and at temperatures ≈ 700 K the contribution of viscosity to the observed sound absorption coefficient does not exceed 20%. For this reason, the high-temperature peaks in $\alpha(T)$ are probably associated with structural relaxation. It follows from the experimental data that the relaxation time of the process is long, constituting 10^{-8} – 10^{-9} sec, and decreases rapidly with increasing temperature. Thus, $\tau(T = 725 \text{ K})/\tau(T = 700 \text{ K}) = 2$. On the basis of the structural properties of the melt and the large values of τ , we note, without discussing all possible relaxation mechanisms, that one of the simplest possible mechanisms could be the model according to which vibrations of the structural units—chains and rings—arise under the action of deformation in an elastic wave. These vibrations are damped due to interaction of the vibrating chains or rings with their environment, and this results in a relaxation process. If it is assumed that some pinning points are present, then we arrive at the string model employed for describing sound absorption in polymer solutions (see the review in Ref. 32).

The relaxation time for such a process can be estimated from the formula³²

$$\tau_B = Bl_{ch}^2/3k_B T,$$

where B is the coefficient of friction and l_{ch} is the length of vibrating chain between the pinning points. If we use for τ_B the values found experimentally and take $B \approx \eta/l_{ch}$, then we obtain for l_{ch} entirely reasonable estimates $(6-10) \cdot 10^{-10}$ m, i.e., such a chain consists of 4–5 atoms. Nonetheless, there are not enough experimental data in order to interpret reliably the high-temperature relaxation mechanism in liquid Se and S with chain-like short-range order.

1.2.5. Effect of melting on the acoustic properties of monatomic substances

It is obvious from what we have said above that the melting, “including” translational motion, drastically changes the dissipative processes responsible for sound absorption. In low-viscosity liquids at frequencies which can be realistically attainable in acoustic experiments it is pointless to estimate the change in the shear modulus. For this reason, the bulk modulus, which remains meaningful in both the solid and liquid states, plays a central role in determining the role of melting in the change in the acoustic properties.

Here it is useful to consider two aspects. On the one hand, there is the role of the translational motion, appearing on melting, of all atoms (structural units), which can be judged by comparing the bulk moduli of amorphous materials and the corresponding melts. On the other hand, melting destroys the long-range order in crystals. The contribution of this process is evidently revealed by comparing the bulk moduli of melts and corresponding crystals at $T \approx T_m$.

It is difficult to answer unequivocally the first of these questions for at least two reasons. First, because of the non-equilibrium nature of the amorphous state, as noted above, the numerical values of the elastic moduli depend on the technology employed for preparing the sample. Second, many alloys which have been studied in the amorphous state have not been studied at temperatures above the melting point. Nonetheless, the experimental facts which have been accumulated (Table IV) permit drawing certain conclusions. In order to be able to ignore relaxation processes, we confine our attention to low-viscosity melts.

Data taken from Refs. 15, 18, and 20 and converted to the melting temperature with typical TCB of $(2-3) \cdot 10^{-4} \text{ K}^{-1}$ are employed in the first column of the table. Since there is no information for the corresponding metallic alloys, the elastic moduli in the liquid state were calculated for melts with close chemical composition from measurements of the speed of sound performed in Refs. 115 and 116. As one can see from Table IV, the appearance of dynamical disorder in melts does not result in any significant change in the bulk

TABLE IV. Changes in the bulk modulus of amorphous substances on melting.

Substance	$K_{AM} \cdot 10^{-10}, \text{Pa}^{1)}$	$K_{liq} \cdot 10^{-10}, \text{Pa}^{2)}$
Fe ₈₀ B ₂₀	10,1 [15]	—
Fe	—	10,8 [116]
Fe ₆₀ Ni ₂₀ B ₂₀	13,6 [15]	—
Fe ₄₀ Ni ₄₀ B ₂₀	11,2 [15]	—
Fe ₈₀ Ni ₂₀	—	11,1 [116]
Fe ₆₀ Ni ₄₀	—	11,4 [116]
Fe ₄₀ Ni ₆₀	—	12,7 [116]
Co ₈₅ P ₁₅	11,7 [15] ³⁾	—
Co	—	12,4
Ge	2,5/2,9 ⁴⁾	3,6 [91]
Si	2,4/3,0 ⁴⁾	3,9 [91]
Se	0,83 [20]	0,48 [110]
Si O ₂	3,7 [20]	14,7 [137]

¹⁾The bulk moduli at $T = 293 \text{ K}$ are presented.²⁾The bulk moduli at T_m are presented.³⁾The values were calculated from the measured shear modulus with a Poisson ratio 0.35.⁴⁾See remark 2) in Table I.

modulus. This result is entirely consistent, both because melting does not result in a significant change in $g(r)$ as compared with the amorphous state, and because the contribution of translational motion to the resulting bulk modulus, calculated from formulas for an ion gas having the density of the real melt (see Ref. 1), does not exceed several percent. In addition, the metallic bond realized by the collectivized electrons is probably insensitive to the translational motion which arises, since diffusion is realized by ions and the time for establishing and breaking bonds does not affect the residence lifetime of an ion.

In the case of elementary semiconductors and dielectrics (Ge, Si, SiO₂), the bulk modulus increases on melting, though, as before, the parameters of short-range order of the amorphous and liquid states are close. It is difficult to associate such an increase in the bulk modulus to the appearance of a metallic type bond due to active translational motion, since the metallic bond, as noted above, under otherwise equal conditions, gives lower values of the bulk moduli than a covalent bond between atoms in amorphous Ge and Si (Table V). This increase in K probably indicates a nonuniform distribution, as noted above, of the free volume in amorphous materials with a covalent bond. By making translational motion possible, melting leads to a uniform distribution of free volume and eliminates bridges with high compressibility between regions with values of K which are normal for a covalent bond.

Thus the existing experimental results show that the appearance of dynamical disorder, as compared with static disorder, in metals is not accompanied by a significant change in the elastic moduli, and in the case of a covalent bond the bulk modulus increases by at least a factor of 1.5.

Since it has been established that the appearance of dynamical disorder in itself at least does not decrease the elastic moduli, we now consider the effect of a loss of short-range order on melting. The basic experimental results on the bulk moduli near the melting point for crystalline and liquid states are summarized in Table V.

The bulk modulus was calculated from the elastic moduli near the melting point for crystals of different symmetry using formulas taken from the monograph of J. Nye.¹³ As

one can see from Table V, the changes occurring in the elastic moduli at melting are very sensitive to loss of long-range order and changes in short-range order. We first consider typical metals, i.e., substances in which the interatomic metallic bond is determining in both the solid and liquid states and which were classified above in group I on the basis of diffraction experiments.

It is easy to see that even in such a group of substances with uniform properties the change in the elastic moduli at melting makes it possible to distinguish two subgroups. The metals Cu, Ag, Pb, Al and others, which are characterized in the solid and liquid states by very close packing and correspondingly coordination numbers close to 11–12, can be put into the first subgroup. In these metals melting and the associated loss of long-range order leads to a small decrease in the bulk modulus by ≈ 10 –15%. Further, in the liquid state they are characterized by a linear decrease in K with increasing temperature.

Metals with more complicated organization of short-range order belong to the second subgroup: In, Sn, and others, including alkali metals. In these metals there are two close coordination spheres in the solid state. After melting these spheres merge, giving a coordination number close to 11–12. Alkali metals also melt with an appreciable increase in the coordination number. Although according to the diffraction experiments there are no significant differences between the structures of the substances in both subgroups, as one can see from the table melting of the metals of the second group is accompanied, in contradistinction to metals of the first group, by a small (5–20%) increase in the bulk modulus.

These characteristics of melting of typical metals, as determined by acoustic methods, are confirmed by results of recent experiments on the positron lifetime in metals in the solid and fused states.¹¹⁸ It has been established that in two metals of the same type Al and In the change in the positron lifetime at melting is different: in Al the lifetime increases and in In it decreases. Since this lifetime in the solid state is determined by vacancy-like defects and in the liquid state it is determined by the free volume, it can be concluded that in Al and In melting changes the packing differently, though in

TABLE V. Comparison of bulk moduli of crystals and monatomic melts near the melting point.

Element	$K_{cr} \cdot 10^{-10}$, Pa	$\frac{1}{K_{cr}} \frac{dK_{cr}}{dT} \cdot 10^4$, K ⁻¹	$K_{liq} \cdot 10^{-10}$, Pa	$\frac{1}{K_{liq}} \frac{dK_{liq}}{dT} \cdot 10^4$, K ⁻¹ 5)	$\frac{\Delta \bar{V}}{\bar{V}_{cr}}$, % 6)	$\frac{K_{cr} - K_{liq}}{K_{cr}}$, %
Na	0,66 ³⁾	—	0,66 [148]	6	+2,8	0
K	0,4 ³⁾	—	0,33 [149]	7	+2,3	—
Cu	11,2 [139]	1,8	9,6 [63]	3,5	+5,5	+15
Ag	7,9 [139]	2,3	6,8 [63]	3,8	+3,4	+14
Pb	3,9 [142]	4,3	3,5 [63]	3,9	+4 [69]	+10
Al	6,2 [147]	3,3	5,3 [150]	3,2	5,2	+15
Sn	4,0 ³⁾	11	4,2 [63]	4	4,2	—5
In	3,6 [142]	7,0	3,8 [64]	2,3	2	—6
Fe	14,7 [141]	1,8	10,8 [116]	3	2,4	+26
Ni	13,8 ³⁾	—	12,9 [116]	3	3,1	+6
Ar	0,18 [143]	50 ⁷⁾	0,09 [135]	80	13	+50
Xe	0,2 [144]	50	0,1 [136]	40	14,4	+50
Cd	2,6 [140]	26	4,7 [64]	2,5 ⁴⁾	+4,1	—81
Zn	2,7 [119]	—	5,3 [64]	2,1 ⁴⁾	+4,0	—96
Bi	2,7 [17]	1,2	2,9 [63]	2)	—1,1	—7
Sb	2,7 [17]	5,1	2,3 [63]	2)	—3,3	+15
Ge	6,2 [17]	1,5	3,6 [91]	2)	—4,8	+42
Si	7,5 [17]	1,0	3,9 [91,95]	1)	—10	+48
Te	1,2 [17]	9,7	0,5 [64]	1)	+5,9	+58
GaSb	5,6 [152]	1,2	3,0 [154]	2)	—8,2	+46
InSb	4,3 ³⁾	1,3	2,7 [154]	2)	—12,5	+37
AlAs	5,9 ³⁾	—	3,0 [154]	2)	—12,9	+49
InAs	5,0 [17]	1,5	4,6 [151]	2)	—7,1	+8
NaCl	1,0 [17]	4,5	1,5 [151]	3,4	25 [153]	—50
KCl	0,8 [17]	13,6	1,2 [151]	5,6	17,3 [153]	—50
KBr	0,9 [17]	9,8	1,1 [151]	5,6	16,6 [153]	—24
KI	0,3 [17]	2,5	0,92 [155]	3,7	15,9 [153]	—200

¹⁾Increases nonlinearly.²⁾Complicated temperature dependence.³⁾Converted from data at room temperature from Ref. 146 with typical values of TCM.⁴⁾Remains constant in a narrow temperature range.⁵⁾The data on β_l were taken from Ref. 59.⁶⁾The data on measurements of the volume of the substance at melting were taken from Ref. 59.⁷⁾Found by combining the data from Refs. 144 and 145.

both cases melting is accompanied by an increase in the specific volume.

These tendencies are even stronger in group-2 metals—Zn, Cd, and Hg, in which on melting the bulk modulus increases by 80–100%. Such a large change in K probably reflects a significant change in the interatomic interaction forces, though melting does not destroy the metallic character of the bond. This question has not been studied theoretically, though, as noted, on the basis of the model of overlapping bonds⁸⁵ the metallic nature of the bonds in bivalent metals is determined by the overlapping of the valence band with a higher-energy band, and this makes their properties depend more strongly on the changes in volume and temperature. In the solid state this was confirmed by measurements of the elastic moduli in a wide temperature range^{119,120} and in the liquid state the speed of sound in Zn and Cd (Ref. 63) behaves nonlinearly with increasing temperature, in contradistinction to the metals examined above, the nonlinearity increasing strongly at temperatures close to the boiling point.

Thus, in metals the loss of long-range order and the appearance of translational degrees of freedom do not change the bond character and the bulk modulus is found to be sensitive only to a change in the short-range order.

However, this behavior is apparently characteristic of

only elements exhibiting a metallic bond. For example, melting of solid inert gases (see Table V), which also does not change the bond character, results in a strong decrease of the bulk modulus. Such a change should reflect the strong dependence of the van-der-Waals bond on the average distance between the atoms.

According to their electrical properties, substances comprising group-3 are in the solid state semimetals (Bi, Sb) and semiconductors (Ge, Si). The most striking feature of the melting of these metals is the reduction in volume, which reflects a significant change in the short-range order. However, the reduction in volume on melting and the increase in the coordination number, as one can see from Table V, is not accompanied by an increase in the bulk modulus. On the contrary, in silicon and germanium it decreases by almost a factor of 2. As noted above, this fact could indicate that melting in these substances is accompanied either by a change in the interatomic interaction potential or by the appearance of an effective relaxation process, giving a large delayed compressibility, or by the appearance of both factors simultaneously. The analysis made above leads to the conclusion that the change in the character (metallization) of interatomic bonds is responsible for the change in the bulk modulus at melting.

According to the acoustic properties, melting proceeds

similarly in $A^{III}B^V$ semiconductor compounds, in which the transition into the liquid state is accompanied by an increase in density and metallization of the interatomic bonds.⁵⁹ Structural studies and molecular-dynamics modeling in liquid GaAs also reveal much in common with elementary semiconductors: finiteness of the lifetime of interatomic bonds; two types of interatomic bonds—metallic and covalent-slightly ionic; high probability (27%) of interaction of pairs of identical atoms, which gives rise to the presence of relaxation processes responsible for the decrease in the bulk modulus at melting, in spite of the decrease in free volume. In elementary semiconductors and semiconductor compounds, which melt by the semiconductor-semiconductor process, in liquid and solid states the short-range order is organized in a complicated manner. Intensive translational motion, which destroys the short-range order by fluctuations, changes the character of the interatomic interaction, injecting into it a metallic component. As a result, the jump in the bulk modulus at melting is different in magnitude and sign, since the change in the instantaneous bulk modulus and the relaxation processes which arise also contribute to it. This situation is reflected in the complicated temperature dependences of the acoustic properties.^{91,93,94,105,121}

Melting in alkali-halide crystals increases the bulk modulus by a factor of 1.5–2 (see Table V), though in contrast to semiconductors the transition into the liquid state is accompanied by a decrease of the density. The character of the interionic bonds at melting probably does not change. In any case, in the melted state salts remain insulators, and the character of the conductivity remains ionic. The bulk modulus of alkali-halide crystals is estimated with the help of the well-known expression¹²²

$$K = \frac{(ze)^2 \gamma_M N_A}{9 \tilde{V} r_{min}} \left(\frac{r_{min}}{r_{exp}} - 2 \right), \quad (51)$$

where γ_M is Madelung's constant, ze is the ion charge, r_{min} is the shortest interionic distance, and r_{exp} is the exponent in the repulsion energy due to overlapping of the shells of positive and negative ions.

In principle, Eq. (51) is also valid for the melt and can be used for estimating the instantaneous modulus of elasticity with the Madelung constant replaced by some liquid-state equivalent γ'_M . For us it is important that there is no basis for assuming that γ'_M differs appreciably from γ_M . The intense translational motion appearing at melting and creating a relaxation process and correspondingly an additional delayed compressibility should decrease the resulting bulk modulus, which does not agree with experiment. For this reason, the significant increase in K at melting can be understood if it is assumed that ze increases in the liquid state, i.e., charged complexes arise in the melt.

We note that irrespective of the results of acoustic experiments a number of properties of fused alkali-halide metals can be explained on the basis of the model of an autocorrelation structure of the melt, in which the melt is considered to be a system of elementary cations and complex halide anions $MeMt^{n-1}$ (Me is a metal and Mt is a metalloid; $n = 1.2-6$). By displacing the equilibrium between complexes, a sound wave gives rise to a relaxation process, leading to excess

sound absorption (as compared with viscous sound absorption), which is observed experimentally.

In principle, it is not difficult to find a concentration of complexes with which it is possible to describe the experimental temperature dependences $K(T)$ and $\alpha_m(T)$ in both order of magnitude and variation as a function of temperature. For purposes of the present analysis, it is only important to note that in the case of melts with ionic bonds the acoustic properties remain highly sensitive to the organization of short-range order in liquids.

Thus the change in the bulk modulus at melting reflects, most uniquely, the changes in the organization of short-range order, if at melting the interatomic interaction remains metallic.

When the character of the interatomic interaction changes, the character of the short-range order also changes, and this makes it difficult to separate these contributions to the jump in the bulk modulus and requires analysis of the temperature dependences $K(T)$ and $\alpha_m(T)$, which are sensitive to the kinetics of the order and disorder processes. We also note that in many cases ΔK_m at melting is more informative than, for example, the change in volume at melting, which is often regarded as a measure of the free volume that appears and is responsible for the kinetics in liquids, or the change in the electrical resistance. For example, the volume of metals belonging to group I of Mendeleev's table Cu, Ag, and Au increases on melting, just as in the case of group-2 metals Zn, Cd, and Hg. The jump in the electrical resistance on melting is close to 2. However, in these metals ΔK_m have different signs, which is an indication that the effect of the increase in volume on the physical properties of both types of substances is not equivalent.

The study of the temperature dependence $\alpha_m(T)$ also makes it possible to determine the change in the interatomic potential and short-range order, which cannot be determined by other methods, in particular, in melted semimetals and semiconductors.

1.2.6. Effect of chemical short-range order on the acoustic properties of melts

In the case of an isotropic interatomic interaction potential of monatomic liquids the short-range order is determined mainly by geometric factors. As a rule, this situation is most clearly realized in close-packed, group I fused metals, i.e., metals with a small free volume. They are characterized in the acoustic properties by a linear decrease of the bulk modulus with increasing temperature and a monotonic increase of the excess sound absorption coefficient.

On the other hand, the appearance of intense translational motion in the liquid state sharply decreases, as compared with the solid state, the characteristic times of the autocorrelation function of the velocity of the atoms. In the case of small free volume this results in the fact that in monatomic melts of metallizing group III semimetals and semiconductors, the short-range order is affected by, in addition to a purely geometric factor, the possibility of realization of two types of interatomic interaction—covalent, characteristic for the solid state, but requiring a long establishment time, and metallic. As a result, the entropy of the system decreases compared with the case of a single type of interatomic interaction; this can be interpreted as manifestation of chemical ordering in addition to geometric ordering. How-

ever, estimates of instantaneous elastic moduli within the hard-sphere model^{70,71} (geometric close-range order) give for bismuth and antimony values which are close to the experimental values, and the specific nature of the organization of the short-range order is reflected in the nonmonotonic temperature dependences of the bulk modulus (speed of sound) and excess sound absorption coefficient. In the presence of a large free volume (liquefied inert gases) or more complicated types of interatomic interaction (for example, liquid selenium) the realization of short-range order is no longer as unique and its manifestation in acoustic properties in each case requires a special analysis (the acoustic properties of liquefied inert gases are reviewed, for example, in Refs. 122 and 123). In all monatomic liquids the most universal and simplest method of changing the short-range order in order to determine its contribution to the acoustic properties is to change the temperature. It is the temperature dependences $K(T)$ and $\alpha_m(T)$ that are most informative, since it is impossible to establish a correlation between the absolute values of the acoustic characteristics and the characteristic features of short-range order (see the above discussion). Of course, experiments involving a change of the external pressure are very helpful, but technically they can be more complicated than experiments in which the temperature is changed.

As mentioned above, in disordered systems there also exists a different type of ordering—chemical ordering, when the character of the short-range order is determined by the chemical interaction between atoms of different types.

The most versatile method for studying the role of chemical ordering in the acoustic properties of liquids is apparently to study systems consisting of different atoms. Here, the role of the chemical factor in short-range order can be determined in a standard manner by studying the plot of an acoustic property as a function of the composition in systems in which a chemical compound is formed at certain concentrations of the components. The physical mechanism of the manifestation of the formed chemical compound in the acoustic properties is obvious and, similarly to monatomic melts, it is associated with the appearance of molecular forms, which reduces the entropy of a binary system and changes its internal energy.

This question was investigated in detail by V. M. Glazov and S. G. Kim and their colleagues on a large number of binary systems, in which under certain conditions a chemical compound is formed, in this case, metal-metal, metal-semimetal, and metal-semiconductor pairs.^{105,124-127} They found that irrespective of the type of interatomic interaction, as in the case of monatomic melts, the establishment of chemical short-range order is manifested primarily in the change in the temperature dependences of the acoustic properties. This is most clearly seen in the TCS as a function of the composition plots, in which the point at which the chemical compound appears is a singular point. Depending on the properties of the components, a maximum or a minimum of the TCS can be observed. The extremum lies in the region $TCS > 0$ or $TCS < 0$ (Fig. 13).^{126,127} This is undoubtedly closely connected with the type of interatomic interaction, but these questions have not been studied in detail.

According to existing experimental data on the manifestation of chemical short-range order in the acoustic properties, the structure of the molecular formation becomes

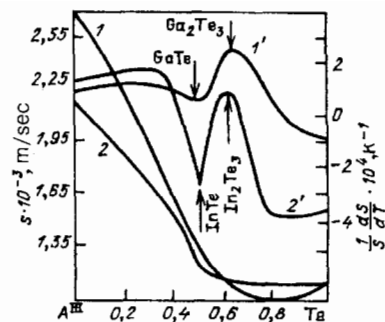


FIG. 13. Concentration dependences of the speed of sound (1, 2) and TCS (1', 2') in GaTe and InTe melts, respectively.

more complicated, the relaxation contribution increases, i.e., if in the binary system the formula of the chemical compound is $A_m B_n$, then as m and n increase, the relaxation corrections to the sound absorption coefficient and the bulk modulus increase. This is illustrated in Fig. 14, which was constructed using the data of Refs. 121 and 125, where the binary systems Ga-Te and In-Te were investigated; in these latter systems, chemical compounds with $m = 1$ and $n = 1$, and $m = 2$ and $n = 3$ can form (the viscosity values required for calculating the classical sound absorption were taken from Ref. 59). Similar results also follow from experiments performed on fused salts, for example, CuCl and CuCl₂, CuBr and CuBr₂.¹²⁸ The differences between $\alpha_m(T)$ in $A_1 B_1$ and $A_m B_n$ reach their maximum values near the melting point. Then they decrease with increasing temperature, so that, for example, in InTe and In₂Te₃ α_m are identical at temperatures ~ 100 K above the melting point. At these temperatures, the TCSs are also identical in both melts. The physical mechanism of relaxation is now similar to that studied for fused elementary semiconductors—modulation of the equilibrium concentration of complexes by an elastic wave. Then, in accordance with the general ideas elaborated above, these experimental results can be interpreted as being

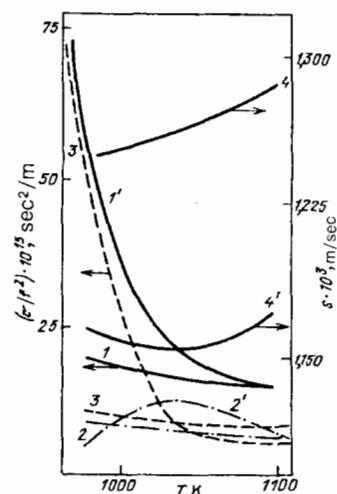


FIG. 14. Same as Fig. 2 but for liquid indium tellurides (the unprimed numbers refer to InTe).

a consequence of the fact that the intensification of thermal motion decreases the lifetime of the compounds $A_m B_n$. For this reason, the equilibrium concentration of such complexes as well as the relaxation sound absorption also decrease.

When the time required to establish a covalent bond becomes less than the lifetime of a complex, chemical ordering of this type vanishes. Thus, the results of acoustic changes indicate that chemical ordering in liquids is of a dynamical character.

Existing data make it possible to estimate the lifetime of the complex In_2Te_3 . If it is assumed that at temperatures $T > 1050$ K the chemical compound In_2Te_3 (see Fig. 14) is not formed, then the contribution Δs to the speed of sound in In_2Te_3 due to relaxation of the concentration of the complexes In_2Te_3 can be calculated by comparing the speed of sound in InTe and In_2Te_3 , for example, at 1100 K and at temperatures near the melting point. On the other hand, it is easy to calculate the difference in the excess absorption in both melts and, using Eq. (33), to calculate τ_{life} , which is found to be $\approx (5-6) \cdot 10^{-11}$ sec.

Similar processes can occur at higher temperatures in InTe as well as in In_2Te_3 melt, but with the compound InTe , since the formation of the latter compounds requires shorter times and therefore they remain at higher temperatures. Estimates of the lifetime of the complexes InTe from acoustic data give $5 \cdot 10^{-12}$ sec.

Thus the dynamics of chemical ordering can be studied by studying the acoustic properties.

2. SOME TECHNICAL APPLICATIONS OF HIGH-TEMPERATURE ACOUSTICS

Many of the results presented above can form a basis for methods of technical diagnostics of the quality of crystals, parts made of amorphous materials, and metallurgical technology. In some cases, for example in the control of metallurgical processes on the basis of measurement of structure-sensitive acoustic properties of melts in order to prepare materials with prescribed properties, only the fundamental possibility is at the present time obvious and significant efforts are required in order to develop practical methods. In other cases, for example in checking heat-treatment of amorphous materials, the methods of making such checks are completely obvious.

However, there exist situations when the development of a diagnostics method involves a definite nontrivial specification of the results presented. As examples we now examine the determination of the components of strain tensors of a crystal lattice strained by a point defect¹²⁹ and the determination of electrical nonuniformities in semiconductor crystals.¹³⁰

The retrieval of the strain tensor is based on the expression (28) from Ref. 1 for the sound absorption coefficient as a function of the direction of propagation of elastic waves and the orientation of the polarization of the waves with respect to the crystallographic axes.

It is easy to see that the sound absorption coefficient determined by the impurities is sharply anisotropic. Its orientational dependence is determined by the tensor $\Omega_{ik}^{(p)}$. For this reason, the study of α for different types of waves propagating in different crystallographic directions can make it possible to estimate the character of the distortions produced in the lattice by impurity atoms.

Measurements of the sound absorption coefficient¹³¹ were performed in a number of bcc metallic single crystals (V, Nb, Mo, W) at frequencies of 10^7 – 10^8 Hz and high temperatures. Extending the temperature range of the investigations up to 1200 K made it possible to observe the relaxation maxima at high frequencies. Under these conditions the medium can be regarded as being infinite and excitation of volume waves—longitudinal and shear waves—is possible in the same samples with characteristic dimensions of ≈ 10 mm. This makes it possible to estimate the components of the tensor $\Omega_{ik}^{(p)}$.

The experimental results obtained reduce to the following. In single crystals of bcc metals there exist a number of directions in which volume elastic waves do not interact with impurities. These include directions along the spatial diagonals (of the type $[111]$), for longitudinal and shear waves; directions along the edges of the cube (of the type $[100]$), for shear waves; directions along the diagonals of the faces (of the type $[110]$), for slow shear waves. In other crystallographic directions these waves are absorbed efficiently. The magnitude of the barrier associated with the displacement of impurities along the lattice can be estimated from the temperature shift of the position of the maxima of the sound absorption coefficient as a function of the frequency. This makes it possible to classify impurities.

The temperature dependences $\alpha(T)$ were obtained for a single crystal of Fe + 3% Si, in which carbon atoms embedded in the initial lattice of the crystal correspond to the size of the potential barrier of the impurity. One of the possible types of defects produced by an impurity atom are distortions with tetragonal symmetry (the impurity is localized on the edges of the cubic unit cell), for which the components of the tensor $\Omega_{ik}^{(p)}$ have the form

$$p=1 \begin{vmatrix} \Omega_1 & 0 & 0 \\ 0 & \Omega_2 & 0 \\ 0 & 0 & \Omega_2 \end{vmatrix}, \quad p=2 \begin{vmatrix} \Omega_2 & 0 & 0 \\ 0 & \Omega_1 & 0 \\ 0 & 0 & \Omega_2 \end{vmatrix},$$

$$p=3 \begin{vmatrix} \Omega_2 & 0 & 0 \\ 0 & \Omega_2 & 0 \\ 0 & 0 & \Omega_1 \end{vmatrix}.$$

It is easy to see that the experimental results are not consistent with such a tensor $\Omega_{ik}^{(p)}$. Indeed, since the edges of the cubic unit cell are the principal axes of the tensor $\Omega_{ik}^{(p)}$, for all shear waves $i \neq k$ $\Omega_{ik}^{(p)} u_{ik} = 0$, i.e., there should be no sound absorption due to impurities.

It can be shown that the symmetry of a cubic lattice admits, besides defects with tetragonal symmetry, also defects with trigonal and orthorhombic symmetries. For trigonal symmetry $\Omega_{ik} = \Omega_4$ ($i = k$) and $\Omega_{ik} = \Omega_5$ ($i \neq k$), where Ω_4 and Ω_5 are some quantities characterizing the deformation of the lattice accompanying the introduction of a defect. It is obvious that defects with trigonal symmetry also cannot explain the experimental results.

It follows from the general formula (28) from Ref. 1 that defects of this type should not contribute to absorption of longitudinal sound in the direction of an edge of the cubic cell, and this disagrees with experiment. The sound absorption coefficient in the $[111]$ direction calculated for trigonal

defects (see Eq. (28) from Ref. 1) is found to be different from zero, likewise in disagreement with experiment. The symmetry of a cubic crystal admits defects with orthorhombic symmetry of two forms of the type [100] and [110]. For the first type, the main symmetry elements are planes and directions parallel to the three axes of the cube and for the second type the main symmetry elements are directions parallel to the diagonals of the faces. For an orthorhombic defect of the first type, for example [100], the components of the tensor $\Omega_{ik}^{(p)}$ have the form (for $p = 1$)

$$\begin{vmatrix} \Omega_1 & 0 & 0 \\ 0 & \Omega_2 & 0 \\ 0 & 0 & \Omega_3 \end{vmatrix}. \quad (52)$$

It is easy to see that the strain tensor of the form (52) for a lattice deformed by impurities makes it possible to interpret the measurements on longitudinal and shear waves in the propagation directions [100] and [111], while for shear waves propagating in the [110] direction this tensor is unsuitable. Indeed, since the edges of the cubic unit cell of the crystal lattice are not "natural" for writing the strain in an ultrasonic wave in the [110] direction, a transformation must be made from one coordinate system (where the strain is given) into another (where the components of $\Omega_{ik}^{(p)}$ are given). The transformation of one coordinate system (primed) into the other (unprimed) is made according to the well-known relation

$$u_{ik} = b_{im} b_{kl} u_{m'l'},$$

where $b_{im'}$ and $b_{kl'}$ are the corresponding direction cosines.

For an ultrasonic wave propagating in the [110] direction the "natural" axes will be those axes in which this direction is also the direction of propagation ($1'$), and then the other axis ($2'$) corresponds to the direction $(1\bar{1}0)$ while the $3'$ axis corresponds to the direction $(00\bar{1})$. In these coordinates the fast shear wave is written as $u_{1'3'}$ and the slow shear wave is written as $u_{1'2'}$.

In the coordinate system tied to the edges of the cubic unit cell of the crystal lattice, the strains in the fast and slow shear waves are represented, respectively, by the matrices

$$\begin{vmatrix} 0 & 0 & u_{1'3'} \\ 0 & 0 & u_{1'3'} \\ 0 & 0 & 0 \end{vmatrix} \text{ and } \begin{vmatrix} u_{1'2'} & -u_{1'2'} & 0 \\ u_{1'2'} & -u_{1'2'} & 0 \\ 0 & 0 & 0 \end{vmatrix}.$$

By substituting the last components of the tensor into Eq. (28) from Ref. 1 it is easy to show that the absorption coefficient, due to impurities of orthorhombic symmetry of the type [100], for fast shear waves is equal to zero (in disagreement with experiment).

Impurities having orthorhombic symmetry of the type [110] create in the lattice distortions which can be characterized by a tensor of the form²⁵

$$p = 1: \begin{vmatrix} \Omega_6 & \Omega_7 & 0 \\ \Omega_7 & \Omega_6 & 0 \\ 0 & 0 & \Omega_3 \end{vmatrix}, \quad p = 2: \begin{vmatrix} \Omega_6 & 0 & \Omega_7 \\ 0 & \Omega_3 & 0 \\ \Omega_7 & 0 & \Omega_6 \end{vmatrix},$$

$$p = 3: \begin{vmatrix} \Omega_3 & 0 & 0 \\ 0 & \Omega_5 & \Omega_7 \\ 0 & \Omega_7 & \Omega_6 \end{vmatrix}.$$

Lattice distortions of the last type make it possible to explain all the experimental factors. Substituting it into Eq. (28) from Ref. 1 and performing the corresponding calculations, we find that for a slow shear wave the sound absorption coefficient due to point defects is equal to zero, while for a fast shear wave it is proportional to $(\Omega_7)^2$. The absorption coefficient α in the [100] direction is equal to zero for shear waves and is proportional to $(\Omega_3 - \Omega_7)^2$ for longitudinal waves. There is no sound absorption for longitudinal and shear waves in the [111] direction.

Thus measurements of α for longitudinal and shear waves at high temperatures and frequencies of 10^7 and 10^8 Hz show that impurity atoms embedded in the lattice of bcc metals give rise to distortions having orthorhombic symmetry of the type [110] and not tetragonal symmetry.

The hypothesis that impurity atoms produce in metals with a bcc lattice defects with tetragonal symmetry is based on the following. In such crystal lattices the largest voids are produced in octahedral (at the center of the edge of a cubic unit cell) and tetrahedral (coordinates, for example, $1/2, 0, 1/4$) interstices and, therefore, impurity atoms are embedded at these locations. Since it is observed experimentally that the distortions have orthorhombic symmetry, in the metals investigated pair defects (dumbbells) are evidently most likely in the metals investigated and the embedding occurs near lattice sites, which, generally speaking, agrees with general qualitative considerations for possible defects in lattices of bcc metals.

In the case of semiconductor crystals a typical breakdown of quality is deviation from a prescribed concentration of dopants or parasitic impurities. If the impurities are electrically active, then their presence can produce in space a nonuniform charge distribution of free (and bound) charge carriers, as well as internal electric fields which affect the operation of semiconductor devices. Acoustical diagnostics, based on the interaction of charge carriers with a propagating elastic wave via piezoelectric and strain potentials, substantially supplements electrical diagnostics methods. The physical basis for this is that the propagation speeds of elastic and electromagnetic waves are different (by a factor of $\sim 10^5$), so that the wavelength of the wave interacting with nonuniformities decreases by the same amount and hence geometric dispersion appears much earlier. In addition, since sound absorption by mobile charge carriers is determined by the production of carriers following the wave, the presence of local internal electric fields changes the local velocity of the charge carriers and as a result the electric clusters and the wave become dephased. This affects the sound absorption coefficient. In the case of an electromagnetic wave this dephasing is 10^5 times weaker. For this reason, the electrical conductivity of nonuniform media is sensitive only to the spatial charge nonuniformities (temporal dispersion). Using the formulas (41)–(43) from Ref. 1 to-

gether with the measurements of the electrical conductivity, it is possible to obtain, by means of simple arguments, estimates not only for the mean-square fluctuations of the density of mobile charge carriers, but also the local electric fields.

First, the condition under which a maximum is observed includes the sample-averaged Maxwellian relaxation time $\langle\tau_M\rangle$, determined by the sample-averaged electrical conductivity $\langle\sigma\rangle$; in experiments on measurement of the electrical conductivity as the coefficient of proportionality between the current density and the intensity of the external field the effective electrical conductivity σ_{eff} is determined and as a rule it is less than $\langle\sigma\rangle$ (see, for example, Ref. 33). The effective electrical conductivity σ_{eff} is equal to $\langle\sigma\rangle$ if the measurements are performed at sufficiently high frequencies when

$$\omega\langle\tau_M\rangle \gg 1 + (D\langle\tau_M\rangle/l_n^2)$$

(the notation is explained in Ref. 1). If the experimental value of $\langle\sigma\rangle$ is known from acoustic data, then it is possible to find equations which relate the parameters of the fluctuations. Since they contain two unknowns b_1 and b_2 (or b_3 and b_4), they must be supplemented by the dc or ac values of σ_{eff} , when

$$\omega\langle\tau_M\rangle \ll 1 + (D\langle\tau_M\rangle/l_n^2).$$

In the latter case

$$\sigma_{\text{eff}} = \langle\sigma\rangle [1 - (\sigma_n^2/n_0^2)].$$

Second, by comparing the maximum of the sound absorption coefficient in the sample with the theoretical value predicted for a uniform sample, it is possible to determine qualitatively the relative characteristic dimensions of the fluctuations. In other words, if the measurements of the electrical conductivity σ_{eff} revealed dispersion at comparatively low frequencies in the region where $\omega\langle\tau_M\rangle$ is of the order of unity and acoustic measurements give only a small displacement of the maximum in α as compared with the uniform sample, then we are dealing with very small nonuniformities, which are characteristic for strongly doped, weakly compensated materials. In the opposite case (with respect to the size of the nonuniformities), if the change in the height of the peak in α [see Eq. (42) from Ref. 1] and its displacement [Eq. (43) of Ref. 1] are measured and $\langle\sigma\rangle$ from electrical measurements is taken into account, then the mean-square fluctuations of the internal field and the concentration of current carriers can be calculated.

Third, the absence of dispersion in σ_{eff} and the existence of deviations in the acoustic measurements from the case of a uniform sample indicate that only fluctuations of the internal field are manifested, and they can be calculated directly.

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Translated by M. E. Alferieff