

Sound absorption in metals at high temperatures

M. B. Gitis

All-Union Research Institute for Nondestructive Quality Control Methods and Means

(Submitted February 23, 1974)

Zh. Eksp. Teor. Fiz. 67, 363-375 (July 1974)

Absorption of longitudinal and shear supersonic waves in metals with body-centered or face-centered cubic lattices (V, Nb, W, Mo, Al) is investigated along various crystallographic directions at frequencies in the 15-75 MHz range and temperatures from 300 to 1200°K. At temperatures above 500-600°K the temperature dependence of the sound absorption coefficient cannot be explained by either the thermoelastic or the dislocation mechanism. It is shown that a possible source of high-temperature acoustic losses at megahertz frequencies may be point defects of impurity or thermal fluctuation origin. This explanation agrees with experiment both in order of magnitude and with respect to the temperature and frequency dependences.

The propagation of ultrasonic oscillations in metals and semiconductors at low temperatures has been the subject of many papers^[1], in which a detailed study was made of the interaction between elastic waves and phonons, electrons, dislocations, etc. in the frequency range $10-10^{10}$ Hz. It is important that when the temperature is lowered the contribution made to the total absorption of the sound by the conduction electrons is greatly increased, so that many subtle effects can be observed, based on electron-phonon interactions. Equally well studied was the room-temperature region ($\sim 300^\circ\text{K}$), where the decrease of the conduction-electron mean free path causes a weakening of the electronic mechanism of absorption, and the phonon processes become fundamental, namely the deformation of the phonon distribution function, the dragging of the dislocations by the phonons, etc. On the other hand, investigations of the propagation of elastic waves at megahertz frequencies and at temperatures greatly exceeding room temperature are practically nonexistent. This is due mainly to the experimental difficulties that arise when such measurements are made.

These include the installation of the piezoelectric converter against high temperatures in the measuring chamber, the production of a reliable acoustic contact at high temperatures, etc. It appears that the consequence of the absence of experimental data was also the very small number of theoretical papers in which the singularities of the velocity and absorption of sound in metals and semiconductors at high temperatures were analyzed. The presence in the investigated object of specific mechanisms of interaction with elastic waves facilitates the interpretation of the experimental results. Thus, in^[2] we investigated the relaxation of the electric conductivity in piezosemiconductors, and the contribution of ferromagnetic phenomena to the absorption of sound at high temperatures was studied in^[3]. It is probable the search for general sound-absorption mechanisms at high temperatures is best started with metals having the simplest lattices, namely body- and face-centered, in which it was reliably established that the main contribution to sound absorption in the temperature region $\sim 300^\circ\text{K}$ is made by dislocation and thermal elastic effects.

We have investigated the absorption of sound at frequencies 15-75 MHz in single crystals of niobium, vanadium, tungsten, and molybdenum with bcc lattice, and also in aluminum, which has an hcp lattice, in different crystallographic directions and in the temperature interval 300-1100°K. The measurements were made with both longitudinal and shear waves.

EXPERIMENT

To produce a reliable acoustic contact during the measurements in the entire temperature interval, a procedure described earlier was used^[4]. The investigated sample was placed between the ends of waveguides made of fused quartz. One of the waveguides, with fixed position, could be oriented in angle with the aid of a ball and socket joint, thus ensuring adjustment of the system, while the second sound guide moving along the system axis, served as the clamp for the sample. The end phases of the waveguides and the sample were placed in a special hermetically sealed chamber. Stable acoustic contact without an intermediate liquid was ensured by clamping the moving waveguide to the sample and evacuating the air from the chamber (the chamber vacuum was $\sim 10^{-2}-10^{-3}$ mm Hg). The samples had a cylindrical shape with diameter 12-15 mm and length 15-20 mm. The accuracy of sample orientation relative to the crystallographic directions was $2-3^\circ$.

The surface was finished to a roughness not exceeding 0.03μ , and the end faces were parallel within not more than 1μ . Prior to the measurements, the surfaces of the samples were polished with AP-1 diamond paste. The sound absorption coefficient α of all the samples was measured beforehand at room temperature at appropriate orientations of the sound propagation directions and of the strains in the wave. In the temperature investigations, only the change $\Delta\alpha$ of the sound absorption coefficient relative to its value at room temperature was measured. Measurements of α at room temperatures were performed by the usual pulse procedure. The details of the measurement of $\Delta\alpha$ were described in detail earlier^[4]. After introducing the diffraction corrections the coefficient α of the investigated single crystals was practically independent of frequency within the limits of experimental accuracy ($\sim 15\%$) at room temperature in the interval 15-55 MHz.

At higher frequencies, the sound absorption coefficient increased with frequency nearly quadratically. The independence of α of frequency below 55 MHz indicates that the main contribution to sound absorption of these frequencies, at temperatures $\sim 300^\circ\text{K}$, is made by the dislocations. Consequently, the temperature measurements were limited mainly to this frequency range.

Figures 1 and 2 show the measured changes of the sound absorption coefficient in niobium in the [110] direction for the longitudinal, rapid, and slow shear waves, respectively. Analogous results for vanadium at a propagation direction [100] are shown in Fig. 3. It is easily seen that for longitudinal waves in both single

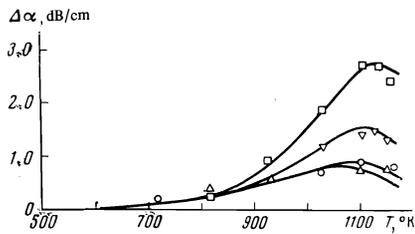


FIG. 1. Temperature dependence of the absorption coefficient of longitudinal waves in niobium in the [110] direction: Δ —15 MHz, \circ —25 MHz, ∇ —55 MHz, \square —85 MHz.

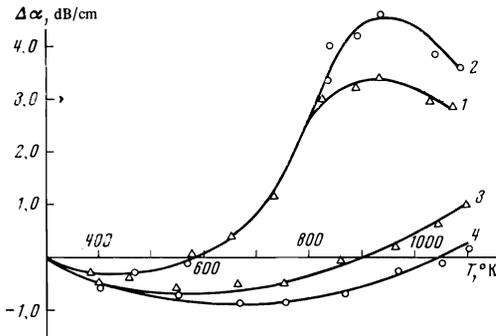


FIG. 2. Temperature dependence of the absorption coefficient of shear waves in niobium in the [110] direction: 1, 2—fast wave, 3, 4—slow wave; Δ —15 MHz, \circ —25 MHz.

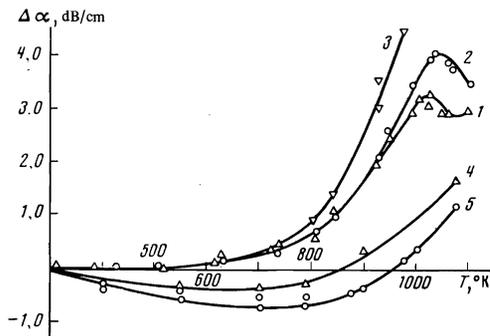


FIG. 3. Temperature dependence of the absorption coefficient of sound in vanadium in the [100] direction: 1, 2, 3—longitudinal waves, 4, 5—shear waves, Δ —15 MHz, \circ —25 MHz, ∇ —55 MHz.

crystals, and also for the rapid shear wave in niobium in the region of 1000°K , a distinct maximum is observed at all the investigated frequencies. The maxima at different frequencies are shifted relative to one another; this shift has a relaxation character, namely, an increase in frequency shifts the maximum towards the higher-temperature region and increases somewhat its height. For the shear waves in vanadium, and also for the slow shear wave in niobium, there was no maximum of sound absorption. Heating above room temperature was in this case first accompanied by a decrease of the sound absorption coefficient; the increase of α started only at sufficiently high temperatures (800 – 900°K). Similar results were observed for longitudinal and shear waves in tungsten and molybdenum in which sound propagated in the [111] direction (Fig. 4).

In all the investigated metals with bcc lattices, the measurement did not lead to disruption of the structure and properties of the samples. In other words, the curves in Figs. 1–4 are average results of numerous measurements made on the sample samples.

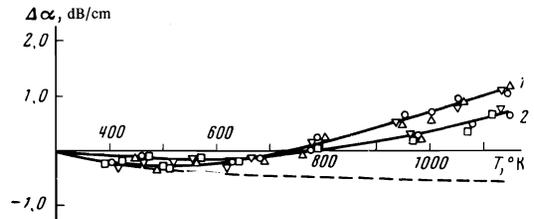


FIG. 4. Temperature dependence of the absorption coefficient of longitudinal waves in tungsten and molybdenum in the [111] direction: 1—tungsten, 2—molybdenum; Δ —15 MHz, \circ —25 MHz, ∇ —55 MHz, \square —85 MHz.

All the investigated metals with bcc lattices have a sufficiently high melting point, much higher than the investigated temperature range. To increase the temperature interval accommodated by the apparatus it would be necessary to replace the fused-quartz waveguides, a difficult task if a small ultrasound damping is to be maintained in the waveguides up to very high temperatures. To investigate the effects at temperatures close to the melting point we have therefore performed measurements in aluminum, a metal with a face-centered lattice ($T_{\text{melt}} = 660^\circ\text{C}$).

Figure 5 shows the results of the measurements in aluminum with longitudinal and shear waves, for sound propagating along the [111] axis. We succeeded in observing here a relaxation maximum in the [111] direction at a temperature $\sim 600^\circ\text{K}$; at low temperatures, just as in the bcc metals, a decrease is noted in the sound absorption coefficient with increasing temperature.

It should be noted that in aluminum, the measurements disturb the acoustic properties of the samples. This may be due to the fact that at temperatures close to the melting point even the low pressures needed to maintain a stable acoustic contact lead to noticeable strains in the sample. We note incidentally that no changes were observed in the acoustical properties of the samples when the measurements were limited to the interval 650 – 700°K . To ascertain whether the observed relaxation maxima are the consequence of deformation of the samples, control measurements were performed, in which a special device was used to increase the pressure on the upper waveguide, and consequently also on the sample, to 3–4 atm. It turned out here that the character of the temperature dependence of $\Delta\alpha$ remained the same, although the height of the maximum decreased to values 0.5–1 dB/cm. Figure 5 shows therefore the average results of single measurements of $\Delta\alpha$ in three samples.

Thus, the results of the experimental investigations in bcc and fcc metals, in the frequency range 15–55 MHz and at temperatures 300 – 1100°K , reduce to the following:

1. In the investigated bcc metals, for strains in the ultrasonic wave in the direction of the body diagonal, one observes first a decrease in the sound absorption coefficient, and then a monotonic increase. There is no frequency dependence in this case.
2. At ultrasonic-wave strains that do not coincide with the body diagonal the absorption coefficient of the sound in investigated metals has a distinct relaxation maximum.
3. In aluminum (fcc lattice), when the strains in the ultrasonic waves are in the direction of the body diag-

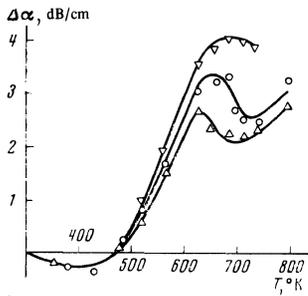


FIG. 5. Temperature dependence of the absorption coefficient of longitudinal waves in aluminum in the [111] direction: Δ —15 MHz, \circ —25 MHz, ∇ —55 MHz.

onal, a relaxation maximum of sound absorption is observed. At slight rises above room temperature, α first decreases; in this temperature region there is no frequency dependence of the sound absorption at 15–35 MHz within the limits of experimental accuracy.

DISCUSSION OF EXPERIMENTAL RESULTS

As is well known, at temperatures on the order of 300°K the main contribution to the sound absorption in metals in the megahertz range is made by thermoelastic and by dislocation losses (a contribution can also be made by the Akhiezer mechanism). In the high-temperature region, however, none of these can explain the temperature dependence of the sound absorption coefficient. Indeed, in the frequency range 10^7 – 10^8 Hz the condition $\omega\tau \ll 1$ (τ is the average relaxation time of the thermal phonons) is satisfied with large margin. Consequently, for the thermoelastic (and Akhiezer) losses we should have $\alpha \propto \omega^2$, something not observed in our experiments either at room temperature or at higher temperatures. Numerical estimates^[1] for the thermoelastic losses yield, for example, for tungsten a value ~ 0.02 – 0.03 dB/cm, and for aluminum in the [111] direction a value 0.1 dB/cm, which amounts to 10–20% of the over-all sound absorption coefficient at 300°K.

Dislocation losses at the investigated frequencies at small deformation amplitudes are connected with the damping of the dislocations, and α_d is expressed in the following manner in terms of the damping constant B , the dislocation density Λ , and the dislocation length L ^[1]:

$$\alpha_d = \frac{Q}{s} \left(\frac{4\mu b^2}{\pi^2 C} \right) \omega_0^2 \Lambda L^2 \frac{\omega^2 d}{(\omega_0^2 - \omega^2)^2 + (\omega d)^2}, \quad (1)$$

where Q is an orientation factor, μ is the shear modulus, b is the Burger's vector, $\omega_0 = \pi L^{-1}(C/A)^{1/2}$, $d = B/A$, A and C are certain constants in the equation of motion of the dislocations, and s is the speed of sound.

The fact that α has no frequency dependence at the frequently obtained large damping ($d/\omega_0 \gg 1$) indicates that $\omega\tau_d \gg 1$ ($\tau_d \equiv d/\omega_0^2$), and the absorption coefficient is in this case

$$\alpha_d = \frac{Q}{s} \frac{4\mu b^2}{\pi^2 B} \Lambda. \quad (2)$$

It is important that under these conditions α_d does not depend on the dislocation-loop length. We shall not dwell here on estimates of Λ and B from (2), inasmuch as at present there are no reliable methods of determining Λ in the volume of a metal, and note only that the values of α measured by us for niobium for longitudinal and both shear waves differ little from the results of Mason and McDonald^[6], who obtained 2.4×10^{-4} dyn-sec/cm².

The temperature dependence of α_d from (2), at constant dislocation density, is determined mainly by the

damping constant. According to Al'tshitz and Mal'shukov^[6], at high temperatures we have

$$B \sim x^4 \int_0^{x^{-1}} \frac{t^4 e^t dt}{(e^t - 1)^2}, \quad x = \frac{T}{\Theta}, \quad (3)$$

from which at temperatures $T \geq \Theta$ (Θ is the Debye temperature), we get $B \propto T$. Consequently $\alpha_d \propto 1/T$. We emphasize that neither the increase of the mobility of the point defects with increasing temperature, nor their diffusion to the dislocations, nor therefore the change of the lengths of the dislocation loops in the considered frequency range ($\omega\tau_d \gg 1$), should change the temperature dependence of α_d . Indeed, for most investigated metals in the temperature interval 300–600°K there is observed a decrease of the sound absorption coefficient approximately like $1/T$. However, further increase of the temperature is accompanied by an increase of α , in contrast to (2). If it is assumed that the increase of α is the consequence of the condensation of the point defects on the dislocations and violation of the condition $\omega\tau_d \gg 1$, then it is difficult to explain the reproducibility of the results of numerous measurements.

To check on the contribution of the condensation of the point defects on the dislocations to the total absorption of the sound in the aluminum samples, we measured the absorption of sound in three samples as a function of the annealing temperature. Within an experimental accuracy of ± 0.2 dB/cm, the results were identical. Similar results were obtained also for bcc metals, in which we observed no dependence of α on the annealing temperature (800, 1000, and 1200°K). It is probable that the growth of the absorption coefficient at high temperatures in metals cannot be satisfactorily attributed to either dislocation or thermoelastic losses, and it is necessary to search for particular high-temperature mechanisms of sound absorption.

One of the causes of sound absorption in metals at high temperatures in the megahertz range may be point defects in the form of impurity atoms. Absorption of sound as a result of impurities in bcc metals has been investigated in sufficient detail^[7] at frequencies 1–10 Hz and temperatures up to 300–400°K. To reveal losses of this type it is necessary that the strain field around the defect have a symmetry different from the lattice symmetry, and this produces in the lattice certain preferred directions. If the defects can be in several equivalent crystallographic positions, and the applied mechanical stress changes the free energy connected with these positions by unequal amounts, then to restore the equilibrium it is necessary to have a suitable redistribution of the defects in the lattice, and it is this which causes the absorption of the sound.

The redistribution of the impurity atoms to new equilibrium positions proceeds via diffusion. Accordingly, the relaxation time τ of this process can be represented in the form $\tau_0 \exp(E/kT)$, where τ_0 is a certain constant proportional to the diffusion coefficient, E is the activation energy of the diffusion motion, and k is the Boltzmann constant. It is obvious that α , which is connected with point defects of this type, should be strongly anisotropic with respect to the applied mechanical stress. According to the experimental results^[7], the activation energy for bcc metals is 20–30 kcal/g-mole, $\tau_0 \approx 10^{-13}$ sec, and consequently the relaxation time τ at temperatures ~ 1000 °K is of the order of 10^{-8} sec. This mechanism may be the cause of the observed relaxation

maxima in niobium for longitudinal and fast shear waves in the [110] direction (Fig. 1), and also in vanadium for longitudinal waves in the [100] direction (Fig. 3).

Estimates of the relaxation time and of the activation energy from the condition $\omega\tau = 1$ and from the temperature shift of the maxima of the curves shown in Figs. 1–3, yield for niobium $E = 33.5$ kcal/mole in the case of measurement with longitudinal waves and $E = 26.4$ kcal/mole for measurements with shear waves, and for vanadium $E = 30.8$ kcal/mole. The results offer evidence that interstitial atoms, probably oxygen atoms, are responsible for the relaxation maxima in the niobium and vanadium, in good agreement with estimates given in [7] for the activation energy of the diffusion of oxygen atoms, obtained at temperatures $\sim 300^\circ\text{K}$ at 0.5 Hz. Somewhat different values of E , obtained from measurements with shear waves in niobium, seem to point to an anisotropy of the activation energy of the diffusion of impurities in lattices of bcc metals. In order of magnitude, the concentrations of the impurity atoms calculated from the height of the maxima of [7] turned out to be $\sim 10^{-4}$ – 10^{-5} for both niobium and vanadium.

However, the redistribution of the impurity atoms under influence of ultrasonic waves cannot explain by itself the entire aggregate of the experimental data. The point is that it is easy to show [7] that at certain ultrasonic-wave strain directions there is no redistribution of the impurity atoms. These directions are, for example, the body diagonals of the bcc and fcc lattices. This case is realized when a slow shear wave propagates in the [110] direction, or a longitudinal wave in the [111] direction. A similar absence of anisotropy occurs for shear waves propagating in the [100] direction. However, the experimental results (Figs. 2–5) point to the existence of an additional sound-absorption mechanism that causes a growth of α with increasing temperature at sufficiently high temperatures, even at the ultrasound propagation directions considered above, and leads even to a pronounced relaxation maximum for aluminum.

Point defects connected with the presence of impurity atoms in bcc and fcc lattices produce in the lattice as a rule [7] a deformation with tetragonal symmetry, when one of the directions of the cube becomes a fourfold axis. This is the reason for the absence of a contribution to the sound absorption in the case of strains along [111]. If we attempt to explain the experimental results by assuming that the point defects constitute an elastic dipole with trigonal orientation (although no such defects have been observed so far in bcc and fcc metals), then a contribution to the sound absorption appears in the case of strains along the body diagonal, but there is no absorption for strains along the axis of the cube [7], which again is in contradiction with experiment.

A possible source of absorption of ultrasonic waves at high temperatures may be thermal-fluctuation defects (vacancies, interstitial atoms, etc.) whose concentration is strongly temperature dependent. In this case, two sound-absorption mechanisms are possible. The first is analogous to that considered above and is connected with the redistribution of the thermal-fluctuation defects in the field of the ultrasonic-wave strains. Accordingly, in order for it to appear, it is necessary that the field of the strains around the thermal-fluctuation defect have a symmetry different from the lattice symmetry. The second is connected with the change of the equilibrium concentration of the thermal-fluctuation defects in the course

of propagation of the ultrasonic wave, i.e., the ultrasonic oscillations modulate the probability of production and annihilation of thermal-fluctuation defects. In principle, the second mechanism should come into play at arbitrary direction of propagation of the ultrasonic oscillations, and its value should increase with temperature. The first to point out the possible contribution to sound absorption by Frenkel vacancies in the megahertz band was Timan [8]. Numerical estimates of the sound absorption as a result of thermal-fluctuation defects can be obtained from the Mandel'shtam-Leontovich relaxation theory [9]. To this end, we modify the customarily employed relations of this theory so as to generalize them to the case of solids.

In the considered case, the relaxing parameter is best chosen to be the concentration of the thermal-fluctuation defects, which varies as a function of the strain and of the temperature in the ultrasonic wave. We note incidentally that it is easy to show that the change of the local concentration of the point defects as a result of pressure and temperature gradient in the wave can be disregarded in the case of metals.

Within the framework of the relaxation theory, the instantaneous changes δc of the local concentration of the point defects are connected with the equilibrium changes δc^e via the relaxation time τ' :

$$\delta c = \frac{\delta c^e}{1 + i\omega\tau'}, \quad \delta c^e = -\frac{F_{cT}}{F_{cc}}\delta T - \frac{F_{cu_{ik}}}{F_{cc}}u_{ik}. \quad (4)$$

Here F is the free energy, u_{ik} is the strain tensor, and the subscripts of F denote differentiation with respect to the corresponding variable. The connection between the relaxation time and the probabilities of creation and annihilation of thermal-fluctuation defects will be discussed later on.

For the isotropic case, expanding the free energy per unit volume in a series, we have (the subscript zero pertains to the unperturbed state)

$$F(T, u_{ik}, c) = F(T, c_0) + \frac{1}{2}Ku_{ii}^2 + \mu(u_{ik} - \frac{1}{3}\delta_{ik}u_{ii})^2 - K\beta u_{ii}\delta T + (F_{Tc})_0\delta T\delta c + (F_{cuk})_0\delta c u_{ik} + \frac{1}{2}(F_{cc})_0\delta c^2, \quad (5)$$

where K is the isothermal elastic modulus, μ is the shear modulus, and β is the coefficient of volume expansion.

Since ultrasonic oscillations can be regarded as adiabatic in the considered frequency region, the adiabaticity condition yields

$$C_V\delta T - T(F_{Tc})_0\delta c + K\beta u_{ii}\delta T = 0, \quad (6)$$

where C_V is the specific heat per unit volume at constant volume. Since the mechanical stress $\sigma_{ik} = F_{u_{ik}}$, we obtain from (5), taking (4) and (6) into account,

$$\sigma_{ik} = K_{ad}\delta_{ik}u_{ii} + 2\mu(u_{ik} - \frac{1}{3}\delta_{ik}u_{ii}) - \frac{1}{C_V C_V} \frac{1}{F_{cc}} (K\beta T\delta_{ik}F_{cT} - C_V F_{cu_{ik}})^2 \frac{u_{ik}}{1 + i\omega\tau}. \quad (7)$$

Here K_{ad} is the adiabatic modulus of elasticity

$$\tau = \tau' C_V / C_{V0}, \quad C_{V0} = C_V + T F_{cT}^2 / F_{cc}.$$

Consequently the sound absorption coefficient is equal to

$$\alpha = \frac{\omega}{2\rho s^3} \text{Im} \frac{\sigma_{ik}}{u_{ik}} = \frac{1}{2\rho s^3 C_V C_V F_{cc}} (K\beta T\delta_{ik}F_{cT} - C_V F_{cu_{ik}})^2 \frac{\omega^2 \tau}{1 + \omega^2 \tau^2}, \quad (8)$$

where s is the speed of sound for the corresponding type of wave and for the corresponding propagation direction, and ρ is the density.

Thus, we can use (8) to calculate α , if we know the dependence of the free energy on the concentration of the point defects.

To calculate α in the anisotropic case it is necessary to modify the expansion (5):

$$F(T, u_{ik}, c) = F(T_0, c_0) + (F_T)_0 \delta T + 1/2 (F_{TT})_0 \delta T^2 + 1/2 \lambda_{ik, mn} u_{ik} u_{mn} - \lambda_{ik, mn} \beta_{mn} \delta T u_{ik} + 1/2 (F_{cc})_0 \delta c^2 + (F_{cu_{ik}})_0 u_{ik} \delta c + (F_{Tc})_0 \delta c \delta T; \quad (9)$$

$$\lambda_{ik, mn} = F_{u_{ik} u_{mn}} \quad \lambda_{ik, mn} \beta_{mn} = -1/2 F_{T u_{ik}}$$

Accordingly, the adiabaticity condition takes the form

$$C_V/T + \lambda_{ik, mn} \beta_{mn} u_{ik} - (F_{Tc})_0 \delta c = 0, \quad (10)$$

whence

$$\sigma_{ik} = \lambda_{ik, mn}^{ad} u_{mn} - \frac{1}{C_V C_V F_{cc}} (\lambda_{ik, mn} \beta_{mn} T F_{Tc} - C_V F_{cu_{ik}})^2 \frac{u_{ik}}{1 + i\omega\tau}, \quad (11)$$

$$\alpha = \frac{1}{2\Omega s^2 C_V C_V F_{cc}} (\lambda_{ik, mn} \beta_{mn} T F_{Tc} - C_V F_{cu_{ik}})^2 \frac{\omega^2 \tau}{1 + \omega^2 \tau^2}.$$

If $c_0 \ll 1$, which is always realized for thermal-fluctuation defects up to the melting temperatures, then a crystal with defects can be regarded as a weak solid solution, in which the defects play the role of the dissolved substance. In this approximation, the free energy per gram-atom of a crystal with defects can be represented in the form [10]

$$F_{u_{ik}=0} = F_{00} + n k T (\ln c - 1) - n \psi(T) \quad (12)$$

Here F_{00} is the free energy of the crystal without defects, n is the total number of defects, and ψ is a certain function of the temperature.

It is easy to show that for thermal-fluctuation defects ψ is constant with good approximation. Indeed, the equilibrium defect concentration, which corresponds to the minimum of F , turns out to equal $\exp(-\psi/kT)$. On the other hand, numerous experimental data on the specific heat and the coefficient of volume expansion at high temperatures (see, e.g., [11]), are well described by the relation $\exp(-\text{const}/T)$.

In a deformed crystal with defects there appears in (12) an additional term of the form $c E_{int}$ [12]. For bcc and fcc crystals in the approximation linear in the elastic deformations we can represent the interaction energy in the form [12]

$$E_{int} = -K \Omega_{ik} u_{ik}, \quad (13)$$

where Ω_{ik} is a symmetrical tensor characterizing the deformation of the lattice as a result of the appearance of a single defect.

Since the volume change due to the appearance of the defect is equal to $\Omega_{II}/3$, it is natural to assume for an interstitial atom $\Omega_{II} > 0$, choosing $\Omega_{II} \sim a^3$, and to assume $\Omega_{II} < 0$ for a vacancy [12]. Consequently, the sound-absorption coefficient due to the thermal-fluctuation defects of one type can be written in the following form: for the isotropic case

$$\alpha = \frac{c}{2s^2 C_V C_V k T} (K \beta k T \ln c \delta_{ik} + K C_V \Omega_{ik})^2 \frac{N}{M} \frac{\omega^2 \tau}{1 + \omega^2 \tau^2}, \quad (14)$$

(N is Avogadro's number and M is the atomic weight), and for the anisotropy case we can write

$$\alpha = \frac{c}{2s^2 C_V C_V k T} (\lambda_{ik, mn} \beta_{mn} k T \ln c \delta_{ik} + K C_V \Omega_{ik})^2 \frac{N}{M} \frac{\omega^2 \tau}{1 + \omega^2 \tau^2}.$$

If the crystal contains simultaneously several types of point defects with respective concentrations c_i , then at $c_i \ll 1$ (which as a rule is realized up to the melting

temperature) we have $\alpha = \sum \alpha_i$. In the investigated high-melting point bcc metals, owing to the large formation energy (several electron volts), the contribution to the sound absorption from the Frenkel defects is small, since their concentration up to temperatures 1200°K does not exceed $10^{-8} - 10^{-10}$. A more probable source of sound absorption at temperatures much lower than the melting point are metastable interstitial atoms crowdion configurations, i.e., atoms that have left "their own" site and have penetrated into the neighboring interstice, causing a slow shift of the surrounding atoms in one of the directions. These configurations turn out to be mobile even at low temperatures, and have a sufficiently low formation energy [13].

If we assume for simplicity that the respective creation and annihilation probabilities A_{cr} and A_{an} per unit time do not depend on the number of the site and interstice and are determined only by the properties of the crystal, then the relaxation time τ' of such a process can be obtained in the following manner: We represent the time dependence of the total number of defects n in the form

$$n = -A_{an} n + A_{cr}(N - n). \quad (15)$$

At equilibrium $\dot{n} = 0$ and accordingly the equilibrium concentration at $n \ll N$ is $c^e = n^2/N = A_{cr}/A_{an}$. The sound wave, by modulating the defect creation and annihilation probabilities, changes the number of defects. Denoting the amplitude of this change by δn , we have, accurate to linear terms

$$\dot{n} \approx -A_{an}(\delta n - \delta n^e). \quad (16)$$

Since $\delta n \sim e^{i\omega t}$, it follows that $\tau' \equiv 1/A_{an}$ and

$$\delta n = \frac{\delta n^e}{1 + i\omega\tau'}, \quad \delta c = \frac{\delta c^e}{1 + i\omega\tau'}. \quad (17)$$

Thus, the relaxation time is determined by the frequency of annihilation of the point defects. The frequency of the transition of the system from one state to the other can be represented in the form $A_{cr} = \nu \exp(-\varphi/kT)$ and $A_{an} = \nu' \exp(-\varphi'/kT)$, where ν and ν' can be treated as the effective frequencies of attempts to overcome the potential barrier, and accordingly $\tau = \tau_0 \exp(\varphi'/kT)$. It should be noted that there are indications [13] that the crowdion configuration becomes metastable at sufficiently high temperatures, and this requires that terms that account for this circumstance be introduced in (15). In addition, it is necessary to take into account in (15), generally speaking, the probability of departure of the defect from its own vacancy, which of course decreases A_{an} . In this case, the calculation of the relaxation time from (15) is modified. However, consideration of these effects is beyond the scope of the present paper, and we shall show that (14) and (15) lead to the correct temperature dependence of α and to a reasonable order of magnitude of the quantities.

In the investigated range of frequencies and temperatures, no frequency dependence of α was observed, thus evidencing satisfaction of the condition $\omega\tau \gg 1$. Therefore

$$c \omega^2 \tau / (1 + \omega^2 \tau^2) = A_{cr}$$

and it is possible to calculate the value of φ from the experimental data. $\varphi = 0.36, 0.29$, and 0.27 eV for tungsten, molybdenum, and niobium, respectively, and these are quite close to kT_{melt} of each metal (0.32, 0.25, and 0.24 eV for tungsten, molybdenum, and niobium, respectively). This agreement is perfectly reasonable, since

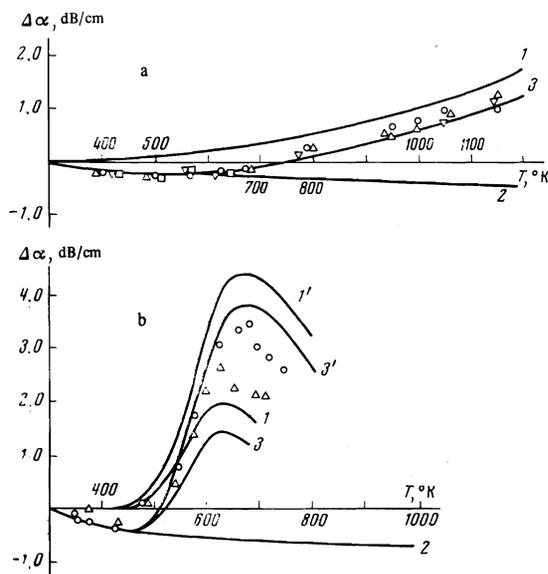


FIG. 6. Theoretical temperature dependences of the absorption of sound for tungsten (a) and aluminum (b). Curves 1 and 1'—absorption due to thermal-fluctuation defects, curve 2—absorption due to dislocations, curves 3 and 3'—absorption due to both mechanisms; curves 1 and 3—15 MHz, 1' and 3'—25 MHz. Points—experimental data corresponding to Figs. 4 and 5; the symbols are the same.

the production of a point defect of the crowdion type is equivalent to "local melting." Figure 6 (curve 1) shows the calculated function $\alpha(T)$ for tungsten with $\varphi = 38$ eV (we assumed in the calculation that $\Omega_{ik}^{1/3}$ is equal to the interatomic distance). Curve 2 corresponds to the dislocation contribution to the absorption of sound and was obtained from the room-temperature values of the absorption coefficient using a temperature dependence in the form $\alpha_d \propto 1/T$. As seen from the diagrams, the agreement between the calculated and experimental values is quite good. Analogous values are obtained also for the other investigated metals.

In the analysis of the experimental results in aluminum it is necessary to take into account the fact that, unlike the bcc metals, the measurement in aluminum were carried out at temperatures close to T_{melt} , and accordingly, in addition to the effects considered above, thermal-fluctuation Frenkel defects can also contribute to the absorption of the sound. Indeed, if we assume $\varphi = 0.1$ eV for aluminum, then the modulation of the probabilities of the production and annihilation of the defects of the crowdion type yields a sound-absorption coefficient that does not exceed 10–15% of the measured value of α .

The change of the Frenkel-defect concentration under the influence of deformations in an ultrasonic wave can occur in principle both as a result of the change in the probability of defects creation and annihilation in accordance with (15), and on account of modulation of the probability of the annihilation of the defects during the course of their random wandering. The contribution of each of these processes to the absorption of sound can be estimated from an analysis of the experimental values of the potential barriers and of the pre-exponential factors.

From (14), the condition that α be a maximum yields

$$\omega\tau = \frac{2\varphi' - \varphi}{\varphi + \varphi'}$$

so that φ' can be determined from the temperature shift of the maxima at the different frequencies. In addition, at low temperatures, where the condition $\omega\tau \gg 1$ is satisfied, we have $\alpha \sim \exp(-\varphi/kT)$. The values obtained in this manner turned out to be $\varphi = 0.9$ eV, $\varphi' = 0.55$ eV, and $\tau_0 = 3 \times 10^{-13}$ sec. The equilibrium defect concentration is

$$c' = \exp\left(-\frac{\varphi - \varphi'}{kT}\right),$$

and yields for the formation energy E_F of the Frenkel-defect (hole–interstitial atom) a value 0.7 eV (The Frenkel-defect concentration calculated directly from the condition that the free energy be a minimum, via the defect-formation entropy, is $\sim \exp(-E_F/2kT)$ ^[11]). The values of E_F obtained from the acoustic measurements agree well with the results of measurements by other methods^[11]. Estimates for τ_0 offer evidence that the main contribution to the sound absorption is made by local changes in the probabilities of the creation and annihilation of the defects, since the annihilation during the random wandering process calls for much longer characteristic times (10^4 – 10^6 jumps).

Thus, within the framework of the thermal-fluctuation mechanism, we can explain the main experimental results on the absorption of sound in bcc and fcc metals at high temperatures, close in order of magnitude and with respect to the temperature and frequency dependences. We note in conclusion that the thermal-fluctuation mechanism of sound absorption in metals at high temperatures is analogous in many respects to the absorption of sound in liquid metals, owing to the structural relaxation^[14]. Relaxation in liquid metals is connected with the change of the structure of the short-range order under the influence of the acoustic waves, and is a direct generalization of the thermal-fluctuation mechanism of sound absorption to include systems in which all the atoms have translational degrees of freedom. Moreover, within the terms of the hole theory of liquids, the structural relaxation is connected with a change in the hole density as a result of deformations in the ultrasonic wave. Consequently, in metals at high temperatures, regardless of the aggregate state, the absorption of sound is due mainly to the change of the local structure as a result of the deformation in the ultrasonic wave.

The author considers it his pleasant duty to thank the participants of Professor I. G. Mikhal'ov's seminar for a useful discussion.

- ¹R. Truell et al., *Ultrasonic Methods in Solid State Physics*, Academic, 1969 (Russ. transl., Mir, 1972).
- ²M. B. Gitis and A. G. Kopanskiĭ, *Fiz. Tverd. Tela* 15, 2941 (1973) [*Sov. Phys.-Solid State* 15, 1962 (1974)].
- ³M. B. Gitis, *Fiz. Met. Metalloved.* 34, 1048 (1972).
- ⁴M. B. Gitis and A. G. Kopanskiĭ, *Akust. Zh.* 18, 381 (1972) [*Sov. Phys.-Acoust.* 18, 320 (1973)].
- ⁵W. P. Mason and D. E. McDonald, *Seventh International Congress on Acoustics*, 21P2, Budapest, 1971.
- ⁶V. I. Al'tshitz and A. G. Mal'shukov, *Zh. Eksp. Teor. Fiz.* 63, 1849 (1972) [*Sov. Phys.-JETP* 36, 978 (1973)].
- ⁷In: *Physical Acoustics*, W. Mason, ed., Vol. 3A, Academic, 1966 (Russ. transl., Mir, 1969).
- ⁸B. L. Timan, *Fiz. Tverd. Tela* 12, 2353 (1970) [*Sov. Phys.-Solid State* 12, 1879 (1971)].
- ⁹M. A. Leontovich, *Zh. Eksp. Teor. Fiz.* 8, 48 (1938).

- ¹⁰L. D. Landau and E. M. Lifshitz, *Statisticheskaya fizika* (Statistical Physics), Nauka (1964) [Pergamon, 1971].
- ¹¹A. C. Damask and G. J. Dienes, *Point Defects in Metals*, Gordon, 1964.
- ¹²A. M. Kosevich, *Osnovy mekhaniki kristallicheskoj reshetki* (Principles of Crystal-Lattice Mechanics), Nauka, 1972.
- ¹³A. Seeger, *Phys. Stat. Sol.* **38**, 235, 1970.
- ¹⁴M. B. Gitis, *Fiz. Met. Metalloved.* **31**, 267 (1971).

Translated by J. G. Adashko
43