The thermal conductivity of glasses at temperatures below the Debye temperature

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A theory is proposed which explains in a unified manner the thermal conductivity of glassy dielectrics from ultralow temperatures to temperatures of the order of the Debye temperature. At low temperatures the thermal conductivity x is due to thermal phonons which are scattered in a resonance manner by two-level systems (TLS):$x \propto T^2$. At temperatures of 10–20 K the $x(T)$ dependence has a plateau which is due to resonance scattering of thermal phonons by anharmonic oscillators, the density of states of which exhibits a van Hove singularity. At still higher temperatures the growth of the thermal conductivity, $x \propto T$, is mainly due to "prethermal" phonons with energies which are much lower than the temperature, scattered resonantly by the TLS. On the other hand, the thermal phonons are scattered resonantly and elastically by quasilocal harmonic-type oscillations (in the present theory their existence in glasses is found to be genetically related to the existence of the TLS); the contribution of these phonons to the thermal conductivity is independent of the temperature. It is shown that this approach can be used to explain the anomalously high values of the phonon-TLS coupling constants observed experimentally.

§1. INTRODUCTION

As is well known, the thermal conductivity of many amorphous dielectrics, semiconductor and metallic glasses, some polymers and superionics at low temperatures, $T \lesssim 1$ K, is proportional to T^2 (Refs. 1–10). This is explained by the scattering of phonons by so-called two-level systems (TLS), the concept of which was introduced independently by Anderson et al[11] and by Phillips[12] (The AHVP model). According to this model there are atoms or groups of atoms in glasses which can exist in two stable equilibrium positions separated by a barrier. This barrier is overcome at low temperatures by quantum-mechanical tunneling.

The AHVP model, in spite of the lack of understanding of the microscopic structure of the TLS, has been very fruitful. It has been possible to explain with its help a whole range of properties of glasses at low temperatures, $T \lesssim 1$ K (see the reviews[13–15]): The specific heat, thermal conductivity, the attenuation, and change of velocity with temperature of ultrasonics, the absorption of microwave radiation, saturation phenomena, echoes, and others. Explanations have been found within the framework of this model for analogous properties of other disordered systems in which TLS have been found: polymers,[9,16,17] superionic conductors,[10,18,19] neutron-irradiated quartz,[20–23] crystals with point defects[24–26] and others (see also Ref. 27).

However, a whole range of universal (i.e. observed in many materials) properties of glasses at higher temperatures—up to several tens of degrees—have so far not received a satisfactory explanation. In particular we refer to the excess specific heat of glasses in comparison with the Debye value and the plateau in the temperature dependence of the thermal conductivity at $T \sim 10$–20 K (Ref. 14) (Fig. 1). The physical reason why the thermal conductivity increases further with temperature at $T \gtrsim 20$ K, according to an approximately linear law, up to temperatures of the order of 100 K, is also unexplained.

Jones et al,[28] have recently proposed an explanation of the observed variations by Rayleigh scattering of phonons for strong dispersion in the transverse acoustic branch. The existence of such dispersion would also explain the correlation between the plateau in the thermal conductivity and the peak in the reduced specific heat $c(T)/T^3$ (see Fig. 1). However, dispersion of high-frequency transverse acoustic phonons was not found by the latest experiments of Rothenfusser[29] for frequencies up to 450 GHz. It follows from this that the excess specific heat of glasses $c(T)$, compared with the Debye value, and the plateau in the thermal conductivity are due to other causes (see also Ref. 30).

In the present work we propose a theory which explains in a unified manner the thermal conductivity of dielectric glasses from infralow temperatures $T < 1$ K up to temperatures of the order of the Debye temperature.[1] Both TLS and additional excitations limiting the high-frequency phonon mean free path come out of it naturally. The additional excitations are quasilocalized harmonic oscillations, the exis-
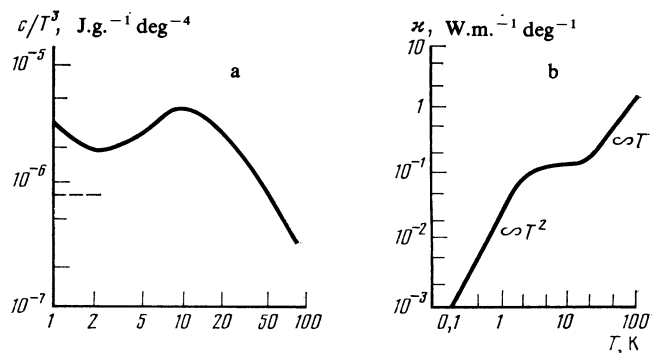

FIG. 1. a) The temperaure dependence of the reduced specific heat c/T^3 of amorphous SiO_2: b) The temperature dependence of the thermal conductivity of the same material.

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tence of which in glasses is found to be genetically related to the existence of TLS.

Our approach is based on considerations of the appreciable role of anharmonicity of local atomic potentials in amorphous systems. Under certain conditions, anharmonicity leads to local atomic potentials becoming double-welled and TLS are created. As will be seen, these conditions correspond precisely to the empirical criterion $E \lesssim 1$ K (where E is the gap between the levels) for the TLS model to be adequate. However, the approach described enables the region of large E to be considered, when the TLS model does not work.

§2. LOCAL ATOMIC POTENTIALS IN AMORPHOUS SYSTEMS

When considering topologically identical structural units of disordered atomic systems, account must be taken of the fluctuation in their parameters. One may be discussing fluctuations of interatomic distances, valence angles etc. The mean values of these parameters, as shown for example by results of x-ray analysis,[33] usually do not differ much from the corresponding values in crystals. The main part of the local atomic potentials in amorphous materials therefore differs little from the crystalline prototype, and has in particular quasielastic constants $k \sim k_0 = M\omega_D^2$, where M and ω_D are the characteristic atomic mass and Debye frequency. However, relatively rare fluctuations are possible for which the local structural parameters are appreciably different from their mean values. Fluctuations with $k \ll k_0$ for local modes of atomic motion are of particular interest. The corresponding atomic potentials were named critical.[34,35] Considering that the magnitude of k is in fact determined by the second derivative of the local potential with respect to the corresponding mode of atomic motion, the existence of fluctuations with $k < 0$ must also be postulated.

For $|k| \ll k_0$ the anharmonicity of the local atomic potentials plays a uniquely important role. The anomalously strong influence of anharmonic effects in amorphous systems compared with crystals, mentioned above, is determined by this.

The critical atomic potentials can be considered effectively single-mode, since the smallness of $|k| \ll k_0$, being a rare event, is realized as a rule for one of the local modes. The rapid oscillations of the other modes (with $k \sim k_0$) are averaged out and only lead to some renormalization of the parameters of the slow motion of the critical mode.[34] As a result, the critical ("soft") atomic potential can be described by the first terms in the expansion,

$$V(x) = \mathscr{E}_0 \left[\eta \left(\frac{x}{a} \right)^2 + t \left(\frac{x}{a} \right)^3 + \left(\frac{x}{a} \right)^4 \right]$$

$$\text{for} \quad |\eta|, \quad |t| \ll 1, \qquad (2.1)$$

where x is a generalized coordinate characterizing the motion, a is a characteristic length of the order of atomic size (~ 1 Å), $\mathscr{E}_0$ is the energy of an atom ($\mathscr{E}_0 \sim \langle M \rangle v^2 \sim 30$ eV, $\langle M \rangle$ is the mean mass of the atoms of the glass, v is the velocity of sound). The dimensionless parameters η and t are considered random quantities and fluctuate from one realization to another. Their distribution functions are shown schematically in Fig. 2. The distribution in t is taken as even,
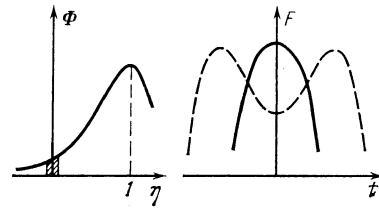

FIG. 2. The distribution functions of the random parameters η and t of an anharmonic oscillator. Shown shaded on the distribution curve $\Phi(\eta)$ is the region with width of the order of η_L of the characteristic scale in η in the problem of the TLS spectrum. The dashed line in the $F(t)$ distribution curve represents an alternative $F(t)$ dependence (full line).

since there are no preferred directions in a glass. The distribution in η corresponds to the hypothesis expounded about the existence, in a glass, of quasilocalized modes with small and even negative values of the local quasielastic constants. The possibility of limiting the expansion of Eq. (2.1) to the first three terms is due to the smallness of the value of x/a for the characteristic values of the parameters η and t [see Eq. (2.3) below] and is related in the final analysis to the softness of the potential $V(x)$.

We note that the random parameters η and t are assumed to be statistically independent. Two other parameters figure in the AHVP model, the asymmetry of the double-welled potential Δ and the height of the barrier λ, which were also considered to be statistically independent. In the approach described, Δ and λ can be expressed in terms of η and t [see Eqs. (3.2), (3.3), (3.5) and (3.7)]. The existence of two random parameters and their statistical independence can be looked on as the empirical requirement of any TLS model.

The spectrum of the potential $V(x)$ is determined from the Schrödinger equation

$$-\frac{\hbar^2}{2M} \frac{d^2}{dx^2} \psi_n + V(x) \psi_n = E_n \psi_n, \quad n = 1, 2, 3, \ldots, \quad (2.2)$$

where M is the effective mass of the moving object, of the order of magnitude of the mean mass of the atoms of the glass $\langle M \rangle$. Enumeration of the energy eigenvalues is in the order of their increase. In order to elucidate the characteristic scale of energies, atomic displacements x and of the parameters η and t, we go over to dimensionless variables in Eq. (2.2) (their characteristic values are of the order of unity)

$$y = x/a\eta_L^{1/2}, \quad \alpha = \eta/\eta_L, \quad \beta = t/\eta_L^{1/2}, \qquad (2.3)$$

where

$$\eta_L = \left(\frac{\hbar^2}{2Ma^2\mathscr{E}_0} \right)^{1/3} \sim \left(\frac{\hbar\omega_D}{\mathscr{E}_0} \right)^{2/3} \sim 10^{-2}. \qquad (2.4)$$

In the new variables, Eq. (2.2) is transformed into

$$\frac{d^2}{dy^2} \bar{\psi}_n + \bar{V}(y) \bar{\psi}_n = \bar{E}_n \bar{\psi}_n, \qquad (2.5)$$

where

$$\bar{V}(y) = w^{-1} V(ay\eta_L^{1/2}) = \alpha y^2 + \beta y^3 + y^4, \qquad (2.6)$$

with the characteristic energy

$$w = \mathscr{E}_0 \eta_L^2 = \frac{\hbar^{4/3} \mathscr{E}_0^{1/3}}{2^{2/3} M^{2/3} a^{4/3}} \sim \hbar \omega_D \eta_L^{1/2} \sim 30 \text{ K}. \qquad (2.7)$$

The E_n spectrum of Eq. (2.2) is related to the $\tilde{E}_n$ spectrum of Eq. (2.5) by the relation

$$E_n = w \tilde{E}_n. \qquad (2.8)$$

The scale of energies[2)] in the potential of Eq. (2.5) is thus $w \sim 30$ K; the characteristic atomic displacements $x/a \sim \eta_L^{1/2} \sim 0.1$.

The boundary lines of the regions for values of the parameters which correspond to different forms of the potential $V(x)$ in the α, β plane are shown in Fig. 3. The unshaded region inside the parabola $\alpha = 9\beta^2/32$ corresponds to single-welled potentials (SP). The shaded region corresponds to double-welled potentials (DP). On the parabola $\alpha = 9\beta^2/32$ and on the β axis, single-welled potentials with a point of inflection (SWI) are realized. Finally, on the parabola $\alpha = \beta^2/4$ and on the semiaxis $\alpha < 0$ symmetrical double-welled potentials (SDP) are realized, the barrier height of which increases with distance from the origin of coordinates. There are naturally points in the region shaded in Fig. 3 at which the form of the potential $V(x)$ is one and the same, corresponding to one and the same spectrum.[3)] These points are connected by the transformations[31]

$$\alpha_{\pm}' = \tfrac{1}{16}[9\beta^2 - 32\alpha \mp 3\beta(9\beta^2 - 32\alpha)^{1/2}],$$

$$\beta_{\pm}' = \tfrac{1}{2}[\pm(9\beta^2 - 32\alpha)^{1/2} - \beta], \qquad (2.9)$$

$$\beta' = -\beta. \qquad (2.10)$$

Using these transformations (see Fig. 3), any point of the shaded region in Fig. 3 (corresponding to DP) can be translated into the quadrant $\alpha < 0, \beta > 0$. This simplifies appreciably the analysis of the spectrum of the potential $V(x)$ (Ref. 31).

It is clear that the observed properties of the quasilocal vibrations considered are determined not only by the spectrum and the structure of the states of the potential of Eq. (2.1), but also by the form of the probability distribution of the random parameters η and t. The question of the scales of the fall of these distributions, $\delta\eta$ and δt are specially important. If they are large in the sense that $\delta\eta \gg \eta_L$ and $\delta t \gg \sqrt{\eta_L}$, then $\Phi(\eta)$ and $F(t)$ can be considered practically uniform distributions, since the wave functions and energies of the potential of Eq. (2.1) change noticeably by an amount of the order of η_L on change of η and t^2 [see Eqs. (2.3) and (2.5)].

Within the framework of the approach described, the scales of $\delta\eta$ and δt should be connected with the characteristic fluctuations of the local structural parameters. Empirical data (see Refs. 33, 36) show that the relative magnitudes of these, θ, do not exceed several percent. However, this does not mean that the quantities $\delta\eta$ and δt are all that small. We shall show that

$$\delta\eta \gtrsim \theta^{2/3}, \qquad \delta t \gtrsim \theta^{1/3} \qquad (2.11)$$

for the condition that the fluctuations in η and t are statistically independent.

Since small $t^2 \ll 1$ are principally realized, it is natural to assume in Eq. (2.1) that there are no systematic reasons for asymmetry and it is a result of the action of weak random fields

$$\mathscr{E}_0 \theta x/a. \qquad (2.12)$$

We will start from the expression

$$V_0 = \mathscr{E}_0 \left[\eta' \left(\frac{x}{a} \right)^2 + \left(\frac{x}{a} \right)^4 \right], \qquad (2.13)$$

which coincides with Eq. (2.1) for $t = 0$. We add the potential (2.12) in Eq. (2.13) and then move the reference point for x so that the coefficient of the linear term should become zero. The value δx of the necessary shift in the reference point satisfies the equation

$$4(\delta x)^3 + 2\eta' \delta x + \theta = 0. \qquad (2.14)$$

As a result of the shift made, we obtain the potential in the form of Eq. (2.1), in which
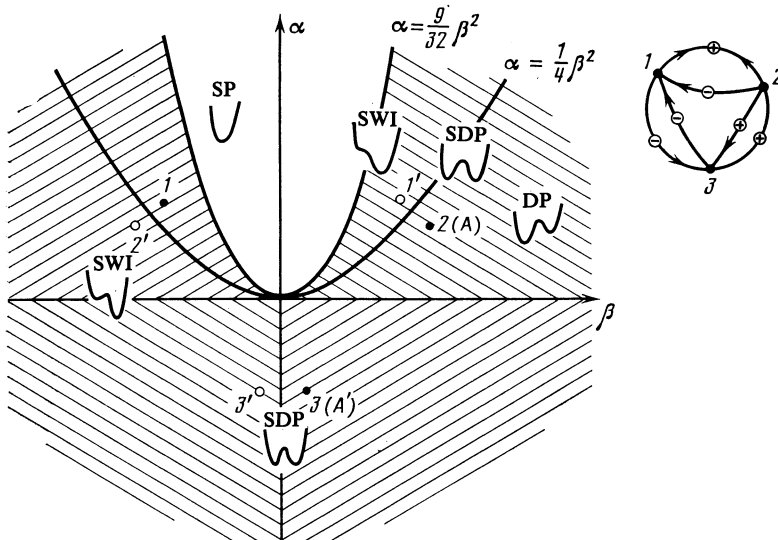

FIG. 3. Lines in the α, β plane which separate regions with values of the parameters corresponding to different forms of the potential $V(x)$ (shown schematically in the insets). Points 1, 2 and 3 correspond to one and the same form of potential $V(x)$. The inset on the right shows by what transformations (see Eq. (2.9) and how the points 1, 2 and 3 in the α, β plane are related among themselves. The open circles 1', 2' and 3' are obtained from 1, 2 and 3 by an inversion transformation $\beta \to -\beta$.

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$$\eta=\eta'+6(\delta x)^2, \quad t=4\delta x. \tag{2.15}$$

If $|\eta'|\ll|\theta|^{2/3}$, then it follows from Eq. (2.14) that $|\delta x|\sim|\theta|^{1/3}$. In the opposite case $|\eta'|\gg|\theta|^{2/3}$ we obtain $|\delta x|\sim|\theta/\eta'|\ll|\theta|^{1/3}$. As can be seen from Eq. (2.15), the values of η and t can be considered to be statistically independent when fluctuations of the parameter η' (arising from other reasons than fluctuations in δx) are larger than or of the order of fluctuations of the quantity $(\delta x)^2$. Equation (2.11) also follows from this.

§3. THE TLS SPECTRUM

Low-frequency phonons, which determine the thermal conductivity of glasses at low temperatures ($T\lesssim 1$ K), are efficiently scattered by TLS corresponding to the two lowest levels of the potential of Eq. (2.1). We shall adduce qualitative considerations establishing the conditions for a TLS to be realized in the potential $V(x)$. Suppose at first that $\eta = t = 0$, i.e., $V = \mathscr{E}_0(x/a)^4$. The first of several interlevel gaps are then of the same order of magnitude ($\sim w$). We now, by reducing the parameter η (for $t = 0$), push out the bottom of the well, forming a barrier. Since the density $|\psi_1|^2$ in the potential x^4 is a maximum for $x = 0$, while $|\psi_2|^2 = 0$, the first level rapidly approaches the second as the barrier grows. The gap between them becomes small (compared with the distance to the third level), when the height of the barrier becomes of the order of or greater than the distance between the first two levels in the potential $V(x)$ for $\eta = t = 0$, i.e of the order of $w\sim 30$ K. The third level then moves up by an amount of the order of w. The condition for a TLS to be formed (unimportance of the third and higher levels) thus has the form

$$E_{21}\equiv E_2-E_1\ll w. \tag{3.1}$$

We note that the condition of Eq. (3.1) corresponds precisely to the empirical criterion $E_{21}\lesssim 1$ K for adequacy of the TLS model.

An analytical dependence of the distance $\widetilde{E}\equiv\widetilde{E}_{21}$ between the first two levels on the parameters of the potential of Eq. (2.6) α and β under the condition in Eq. (3.1) can be obtained if it is noticed that, for $\beta = 0$ and $\alpha < 0$, the potential $\widetilde{V}(y)$ (Eq. (2.6) is an SDP with barrier height $\alpha^2/4$ and distance $(2|\alpha|)^{1/2}$ between the minima. In this case the distance between the first two levels is determined by the tunnel splitting $\widetilde{\Delta}_0$, which for $|\alpha|\gg 1$ is equal (in units of w) to

$$\widetilde{\Delta}_0=\exp\{-(\sqrt{2}/3)|\alpha|^{3/2}\} \tag{3.2}$$

to an accuracy up to the pre-exponential factor.

For $|\alpha| = -\alpha\gg 1$, the potential $\widetilde{V}(x)$ remains double-welled but weakly asymmetric and in the case of finite but sufficiently small values, $|\beta|\ll|\alpha|^{-3/2}$. The energy difference between the minima is less than $\delta\widetilde{V} = 2^{-1/2}|\beta||\alpha|^{3/2}$. To a first approximation the distance between the levels of the ground state energies in isolated wells (the asymmetry $\widetilde{\Delta}$) coincides with $\delta\widetilde{V}$. Then

$$\widetilde{\Delta}=2^{-1/2}|\beta||\alpha|^{3/2}. \tag{3.3}$$

SDP are realized on the α, β plane not only on the semiaxis $\alpha < 0$, but also on the parabola $\alpha = \beta^2/4$ (see Fig. 3).

The points A and A' in the α, β plane (Fig. 3), in which the form of the potential of Eq. (2.6) is one and the same, are connected by the relation of Eq. (2.9) with the plus sign. The point A on the parabola $\alpha = \beta^2/4$ corresponds to point A' situated on the negative semiaxis α, with coordinates

$$\beta'=0, \quad \alpha'=-\beta^2/8. \tag{3.4}$$

The tunnel splitting at $|\beta|\gg 1$ is in this case, according to Eq. (3.2), equal to

$$\widetilde{\Delta}_0=\exp\left(-\frac{1}{48}|\beta|^3\right). \tag{3.5}$$

If the point A is situated near the parabola $\alpha = \beta^2/4$, then the weakly asymmetric DW with

$$\beta'=-8R/\beta, \quad R\equiv\alpha-\beta^2/4, \quad |R|\ll\beta^{-2} \tag{3.6}$$

corresponds to it. For $|R|\ll\beta^{-2}$, α remains constant and is determined by Eq. (3.4). In this case the asymmetry can be represented in the form [see Eq. (3.3)]

$$\widetilde{\Delta}=\tfrac{1}{4}|R|\beta^2. \tag{3.7}$$

We will call two-level systems realized on the semiaxis $\alpha < 1$ type-I TLS and those on the parabola $\alpha = \beta^2/4$ type-II TLS.[34] For both types of TLS the distance between levels is

$$E=w\widetilde{E}, \quad \widetilde{E}=(\widetilde{\Delta}_0^2+\widetilde{\Delta}^2)^{1/2}. \tag{3.8}$$

The dependences of $\widetilde{\Delta}$ and $\widetilde{\Delta}_0$ on the parameters of the TLS are determined by Eqs. (3.2) and (3.3) for a type-I system and by Eqs. (3.5) and (3.7) for type-II systems.

§4. THE COUPLING BETWEEN TLS AND PHONONS. THE TLS DEFORMATION POTENTIAL

The Hamiltonian of an anharmonic oscillator interacting with phonons and with the low-frequency deformation field ε_{ik} can be written in the form

$$H=-\frac{\hbar}{2M}\frac{d^2}{dx^2}+\mathscr{E}_0\left[\eta_0\left(\frac{x}{a}\right)^2+t_0\left(\frac{x}{a}\right)^3+\left(\frac{x}{a}\right)^4\right]$$
$$+d_{ik}\mathscr{E}_0\left(\frac{x}{a}\right)^2(\varepsilon_{ik}+\varepsilon_{ik}^0)+b_{iklm}\mathscr{E}_0\frac{x}{a}(\varepsilon_{ik}+\varepsilon_{ik}^0)(\varepsilon_{lm}+\varepsilon_{lm}^0), \tag{4.1}$$

where η_0 and t_0 are the bare (in the absence of coupling) values of the parameters η and t, ε_{ik} is the deformation of frequency low compared with $w/\hbar$, ε_{ik}^0 is the phonon field of frequency high compared with $w/\hbar$, which for $T\ll w/\hbar$ is the so-called zero-point oscillations of the atoms of the glass, d_{ik} and b_{iklm} are dimensionless tensors with numerical components of the order of unity or of a few units. The last two terms in Eq. (4.1) are the interaction Hamiltonian H_{int} of an anharmonic oscillator with a deformation field. There is no harmonic component of the interaction $x\varepsilon_{ik}$ in the Hamiltonian unrenormalized by phonons, since x is a normal mode of atomic motion.

We average H_{int} over the high-frequency oscillations. The possibility of such averaging is associated with the fact that the motion in soft potentials is slow and takes place with a characteristic frequency of the order of $w/\hbar\ll\omega_D$. Remembering that

$$\langle \varepsilon_{ik}{}^0 \rangle = 0, \quad \langle (\varepsilon_{ik}{}^0)^2 \rangle \sim \hbar \omega_D / \mathscr{E}_0, \tag{4.2}$$

and introducing the notation

$$b_{iklm} \langle \varepsilon_{ik}{}^0 \varepsilon_{lm}{}^0 \rangle \equiv b \eta_L^{3/2} \sim \hbar \omega_D / \mathscr{E}_0, \tag{4.3}$$

where b is a number, we obtain

$$\langle H_{int} \rangle = d_{ik} \mathscr{E}_0 \left(\frac{x}{a} \right)^2 \varepsilon_{ik} + b \eta_L^{3/2} \mathscr{E}_0 \frac{x}{a}. \tag{4.4}$$

The second term in Eq. (4.4) can be removed by shifting the origin for measuring x and redefining the parameters η_0 and t_0:

$$\mathscr{E}_0 \left[\eta_0 \left(\frac{x}{a} \right)^2 + t_0 \left(\frac{x}{a} \right)^3 + \left(\frac{x}{a} \right)^4 \right] + b \eta_L^{3/2} \mathscr{E}_0 \frac{x}{a}$$

$$= w (by + \alpha_0 y^2 + \beta_0 y^3 + y^4)$$

$$= w [\alpha (y - \delta)^2 + \beta (y - \delta)^3 + (y - \delta)^4] + \text{const}, \tag{4.5}$$

where $\alpha_0 = \eta_0 / \eta_L$, $\beta_0 = t_0 / \eta_L^{1/2}$, $y = x / a \eta_L^{1/2}$. The shift δ is determined from the equation

$$b + 2\alpha\delta - 3\beta\delta^2 + 4\delta^3 = 0, \tag{4.6}$$

where the renormalization parameters α and β are related to the sources by the equations

$$\alpha_0 = \alpha - 3\beta\delta + 6\delta^2, \quad \beta_0 = \beta - 4\delta. \tag{4.7}$$

Equation (4.6) determines δ as a function of the renormalization parameters α and β (i.e η and t), just for which the distribution of Fig. 2 occurs.

It can be verified that for both type I and type II TLS (corresponding to $|\alpha| \gg 1$ and $|\beta| \gg 1$), the second term in Eq. (4.6) is appreciably greater than the third or fourth. As a result, it follows from Eq. (4.6) that

$$\delta = -b / 2\alpha. \tag{4.8}$$

This relation can be used directly for type-I TLS, but for type-II TLS it must be expressed in terms of the variables β and $R = \alpha - \beta^2 / 4$.

Finally, the interaction Hamiltonian V_{int} of an anharmonic oscillator with a low-frequency (compared with $w/\hbar$) deformation field ε_{ik} is obtained from the first term in Eq. (4.4), which can be rewritten in the form $w y^2 d_{ik} / \eta_L$. Performing the substitution $y \to y + \delta$, we obtain

$$V_{int} = w \tilde{V}_{int}, \quad \tilde{V}_{int} = \eta_L^{-1} (y^2 + 2\delta y) d_{ik} \varepsilon_{ik}. \tag{4.9}$$

This Hamiltonian describes the interaction of a TLS with the low-frequency deformation field ε_{ik} and leads to the following dependences of the parameters α and β of an anharmonic oscillator [Eq. (2.6)] on ε_{ik} (for $\varepsilon_{ik} \to 0$):

$$\frac{\partial \alpha}{\partial \varepsilon_{ik}} = \frac{d_{ik}}{\eta_L}, \quad \frac{\partial \beta}{\partial \varepsilon_{ik}} = -\frac{4\delta d_{ik}}{\eta_L \alpha}. \tag{4.10}$$

These expressions can be used directly for type-I TLS, by substituting δ from Eq. (4.8) into them. The quantity

$$\partial R / \partial \varepsilon_{ik} = d_{ik} / \eta_L, \tag{4.11}$$

is also required for type-II TLS.

Kinetic phenomena in glasses at low temperatures are determined by the deformation potentials[13]

$$D_{ik} = \frac{\partial E}{\partial \varepsilon_{ik}} = \frac{\Delta}{E} \frac{\partial \Delta}{\partial \varepsilon_{ik}} + \frac{\Delta_0}{E} \frac{\partial \Delta_0}{\partial \varepsilon_{ik}}, \tag{4.12a}$$

$$M_{ik} = \frac{1}{2} \frac{\Delta_0}{E} \frac{\partial \Delta}{\partial \varepsilon_{ik}} - \frac{1}{2} \frac{\Delta}{E} \frac{\partial \Delta_0}{\partial \varepsilon_{ik}}. \tag{4.12b}$$

The first characterizes the change E in the energy of a TLS in a deformation field ε_{ik}, and the second the strength of the coupling of the ground and excited states in a two-level system in a varying deformation field ε_{ik}. It can be shown by using Eqs. (3.2), (3.3), (3.5), (3.7) and (4.10) and (4.11) together with (4.8), that both for type-I and for type-II TLS, the first term in Eqs. (4.12a,b) is w/E times larger than the second. This means that all kinetic phenomena in glasses at low temperatures are determined by the single deformation-potential tensor

$$\gamma_{ik} = \partial \Delta / 2 \partial \varepsilon_{ik}, \tag{4.13}$$

which characterizes the change in the TLS asymmetry in the deformation field. Through it we can express (cf. Ref. 15)

$$D_{ik} = 2 \frac{\Delta}{E} \gamma_{ik}, \quad M_{ik} = \frac{\Delta_0}{E} \gamma_{ik}. \tag{4.14}$$

Differentiating Eq. (3.3) with respect to[4] β and using Eqs. (4.10) and (4.8), we obtain for a type-I TLS

$$\gamma_{ik}{}^I = d_{ik} \frac{b}{6^{1/4}} \frac{w}{\eta_L} \left(\ln \frac{w}{\Delta_0} \right)^{-1/4} \text{sign } t, \tag{4.15}$$

An order of magnitude estimate of γ^I is $w/\eta_L \sim 0.3$ eV, which agrees with values of the deformation potential obtained from experiments on thermal conductivity and sound attenuation.[4,37]

We obtain for a type II TLS in a similar way, by differentiating Eq. (3.7) with respect to R and using Eq. (4.11)

$$\gamma_{ik}{}^{II} = d_{ik} \left(\frac{9}{2} \right)^{1/3} \frac{w}{\eta_L} \left(\ln \frac{w}{\Delta_0} \right)^{2/3} \text{sign } R. \tag{4.16}$$

The ratio of the deformation potentials for types I and II TLS is

$$\frac{\gamma_{ik}{}^{II}}{\gamma_{ik}{}^I} = \frac{3}{b} \ln \frac{w}{\Delta_0}. \tag{4.17}$$

For $w/\Delta_0 = 600$, which corresponds to an actual splitting $\Delta_0 \sim 0.05$ K (or to a frequency $f \sim 1$ GHz), the numerical factor in the numerator of Eq. (4.17) is ~ 20, and it is not impossible that type-II TLS (for not too large b) are coupled appreciably more strongly to phonons than type-I TLS. This confirms the hypothesis, proposed on empirical foundations by Halperin and Black,[38] about the existence of two types of TLS in glasses with different interactions with phonons.

We also note that because of the signum functions which enter Eqs. (4.15) and (4.16), TLS with different signs of deformation potential γ_{ik} should exist in glasses. By this means experiments on the "non-lifting" of the TLS spectrum at high pressures[39] can be explained, and also the contradictions which arise on trying to apply the AHVP model to explain the low-temperature thermal expansion of glasses[40,41] can be removed.

§5. THERMAL CONDUCTIVITY AT LOW TEMPERATURES $T \ll w$

On the assumption that the heat is transported by phonons, we have the following expression for the thermal conductivity:[42]

$$\varkappa(T) = \frac{1}{6\pi^2} \int_0^\infty d\omega\, \omega^2 \left(\frac{\hbar\omega}{2T}\right)^2 \left(\operatorname{sh}\frac{\hbar\omega}{2T}\right)^{-2} \left(\frac{L_l}{v_l^2} + \frac{2L_t}{v_t^2}\right), \qquad (5.1)$$

where L_l and L_t are the mean free paths of longitudinal and transverse phonons, v_l and v_t are the longitudinal and transverse velocities of sound. In anisotropic glass we have the following expression[13] for the mean free path of phonons of frequency ω, scattered in a resonance fashion by TLS with $E = \hbar\omega$,

$$L_s^{-1} = \frac{\pi\omega}{\rho v_s^3} \sum \left(\frac{\Delta_0}{E}\right)^2 \gamma_s^2 \operatorname{th}\frac{E}{2T}\, \delta(\hbar\omega - E), \qquad (5.2)$$

where ρ is the density, $s = (l, t)$ and the summation in Eq. (5.2) is carried out over the TLS in unit volume. The value of γ_s^2 is expressed in terms of the components of the deformation potential tensor γ_{ik} of one TLS:[43,44]

$$\gamma_l^2 = \frac{1}{15}[(\operatorname{Sp}\gamma)^2 + 2\operatorname{Sp}\gamma^2], \quad \gamma_t^2 = \frac{1}{30}[3\operatorname{Sp}\gamma^2 - (\operatorname{Sp}\gamma)^2]. \quad (5.3)$$

It is convenient to go over to the variables E and p for carrying out the summation over TLS in Eq. (5.2):

$$p = (\Delta_0/E)^2. \qquad (5.4)$$

In terms of these variables the density of states $N_{\mathrm{I,II}}(E,p)$ of TLS type I and II is

$$N_j(E,p) = 2^{5/3} 3^{-4/3} G_j \eta_L^{2/3} w^{-1} p^{-1} (1-p)^{-1/2} \left(\ln\frac{w}{Ep^{1/2}}\right)^{-4/3}, \qquad (5.5)$$

where $j = \mathrm{I, II}$ and

$$G_j = \Phi(\eta_j) F(t_j). \qquad (5.6)$$

The characteristic values of the parameters η_j and t_j are weakly (logarithmically) dependent on E and p [see Eqs. (3.2), (3.3), (3.5) and (3.7)]. In what follows we will consider the quantities G_j constant in view of the smoothness of the distributions in η and t.

Integration according to Eq. (5.2) with weight of (5.5) gives

$$L_s^{-1} = \frac{4\pi w d_s^2}{\rho v_s^3 \eta_L^{1/2}}\, \omega \left(\operatorname{th}\frac{\hbar\omega}{2T}\right) \left[\frac{b^2}{9} G_{\mathrm{I}}\left(\ln\frac{w}{\hbar\omega}\right)^{-2} + G_{\mathrm{II}}\right], \quad (5.7)$$

where the first and second terms reflect the contribution from scattering by TLS types I and II. The quantities d_s^2 are determined by the relations [see Eq. (5.3)]

$$d_l^2 = \frac{1}{15}\langle(\operatorname{Sp} d)^2 + 2\operatorname{Sp} d^2\rangle, \quad d_t^2 = \frac{1}{30}\langle 3\operatorname{Sp} d^2 - (\operatorname{Sp} d)^2\rangle, \quad (5.8)$$

where the angular brackets denote averaging over the TLS ensemble with the given value of the energy $E = \hbar\omega$. In deriving Eq. (5.7) it was assumed that the parameters d_{ik} are not correlated with η and t.

Substituting Eq. (5.7) into Eq. (5.1) and integrating over

ω, we arrive at the following expression for the thermal conductivity (at low temperatures $T \lesssim 1$ K):

$$\varkappa(T) = \frac{1}{24\pi}\frac{\rho\eta_L^{1/2}}{\hbar^2 w G_1 b^2}\left(\frac{v_l}{d_l^2} + 2\frac{v_t}{d_t^2}\right)\left(T\ln\frac{w}{T}\right)^2$$
$$\times \left[1 + \frac{9 G_{\mathrm{II}}}{b^2 G_{\mathrm{I}}}\left(\ln\frac{w}{T}\right)^2\right]^{-1}. \qquad (5.9)$$

Equation (5.9) is valid up to a coefficient of the order of unity in the logarithmic term. The temperature dependence in Eq. (5.9) only differs from the results of the AHVP model (which leads to the $\varkappa \propto T^2$ law) in the last factors, which depend logarithmically on temperature. It is possible that they cause the experimentally observed weak departure of the temperature dependence of the thermal conductivity from the T^2 law.[4]

§6. QUASILOCALIZED HARMONIC VIBRATIONS IN GLASSES

Equation (2.1) predicts, besides the existence of strongly anharmonic potentials in which TLS are realized, also the existence of quasilocalized harmonic modes with small quasielastic constants and relatively small anharmonic effects. In the α, β plane (Fig. 3) the regions near the α and β axes correspond to these modes for, respectively, $\alpha \gg 1$ and $\beta^2 \gg 1$. Following the terminology introduced above, they can be called quasilocalized harmonic oscillations of the first (I) and second (II) types. The quasielastic constants

$$k^{\mathrm{I}} = 2\mathscr{E}_0\eta/a^2, \quad k^{\mathrm{II}} = 9\mathscr{E}_0 t^2/4a^2, \qquad (6.1)$$

correspond to them. In the harmonic approximation such potentials have equidistant spectra with interlevel gaps

$$E^{\mathrm{I}} = 2w\alpha^{1/2}, \quad E^{\mathrm{II}} = (3/\sqrt{2})\, w|\beta| \qquad (6.2)$$

and density of states

$$N^{\mathrm{I,II}}(E) = 2\int_{-\infty}^\infty d\eta \int_0^\infty dt\, \Phi(\eta) F(t)\, \delta(E - E^{\mathrm{I,II}}). \qquad (6.3)$$

It must be taken into account, when integrating in Eq. (6.3), that the effects of anharmonicity become appreciable near the line $\eta = t^2/4$ in the η, t plane (Fig. 3). Therefore, $N^{\mathrm{I,II}}(E)$ can be evaluated by limiting the integration over t in Eq. (6.3) in case I to the limits from zero to $2\eta^{1/2}$, and in the second case integrating over η in the limits from zero to $t^2/4$. As a result we obtain for sufficiently smooth $\Phi(\eta)$ and $F(t)$ distributions

$$N^{\mathrm{I}} \approx G\eta_L^{1/2} w^{-3} E^2, \quad N^{\mathrm{II}} \approx 0.05 N^{\mathrm{I}}, \qquad (6.4)$$

where $G = \Phi(0) F(0)$. The density $N^{\mathrm{II}} \ll N^{\mathrm{I}}$, so that in what follows we limit ourselves by considering only type I quasilocal harmonic modes.

For $E \approx w$ the density N^{I} coincides to an order of magnitude with the density of TLS states which is independent of energy [see Eq. (5.5)], as should be expected starting from the continuity of $N(E)$. We note that the existence of quasilocalized harmonic vibrations in glasses is, in the framework of the approach described, genetically related to the existence of TLS.

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§7. THE INTERACTION OF PHONONS WITH QUASILOCALIZED HARMONIC VIBRATIONS. THE THERMAL CONDUCTIVITY AT HIGH TEMPERATURES $T > w$

It is natural to suppose that the quasilocalized harmonic vibrations limit the mean free path of high-frequency phonons with $\hbar\omega > w$ in glasses, decreasing their contribution to the thermal conductivity at $T > w$. The possibility of the existence of weakly attenuated quasilocal harmonic oscillations in imperfect crystals, with frequency falling within the allowed phonon frequency spectrum, had already been predicted theoretically by Kagan and Iosilevskiĭ.[454] The reason for their appearance is either a large mass for the impurity atom or a small quasielastic constant. In glasses it is just the second possibility which is realized. The coupling between soft quasilocalized modes and phonons in crystals has been considered by Krivoglaz and Pinkevich.[46] The mechanism of this coupling in glasses does not differ in principle from that in crystals. Its essence, briefly, comes down to the following.

A soft quasilocal mode is an atom or group of atoms of the glass which are in some degree of freedom weakly bound to the surroundings—the neighboring atoms. The latter are bound together by strong elastic couplings. Therefore as an elastic wave with wavelength appreciably greater than the dimensions of the "softened region" traverse the glass, they move as one unit. The whole construction recalls a harmonic oscillator with a vibrating point of attachment. When the frequency of the sound wave enters into resonance with the frequency of the quasilocal mode, its scattering cross section also grows in a resonant manner.

From what has been said, the Hamiltonian of a soft quasilocal mode interacting with phonons in a inertial frame of reference can be written as

$$H = -\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + V(x - \xi\mathbf{u}), \tag{7.1}$$

where $\mathbf{u}(t)$ is the displacement of the atoms at the point where the quasilocal mode occurs, produced by the phonons, ξ is a dimensionless vector characterizing its spacial orientation. The absolute value of ξ depends on the actual structure of the center and can be of the order of unity or a few units (cf. Ref. 46). To first order in $\mathbf{u}$ the interaction considered is described by the Hamiltonian

$$H_{int} = -(\partial V/\partial x)\,\xi\mathbf{u}, \tag{7.2}$$

which for type I harmonic quasilocalized modes is of the form

$$H_{int} = -k^{\mathrm{I}}x\xi\mathbf{u}. \tag{7.3}$$

For harmonic high-frequency quasilocal modes with $E > w$, Eq. (7.3) is the main interaction and is much more effective than interaction by means of the deformation potential, considered in §4. On the other hand, for TLS with appreciably anharmonic soft potentials, the interaction of Eq. (7.2) is negligibly small compared with that considered in §4. This follows from the identity

$$\langle n|\frac{dV}{dx}|m\rangle = (E_m - E_n)\langle n|\frac{d}{dx}|m\rangle = \frac{M}{\hbar^2}(E_m - E_n)^2\langle n|x|m\rangle, \tag{7.4}$$

where $|n\rangle$ and $|m\rangle$ are states in the potential $V(x)$. It can be seen from Eq. (7.4) that the contribution to the transition probability from the interaction of Eq. (7.2) is small through the parameter $E/w \ll 1$, where E is the small energy gap of the TLS, compared with the contribution from the interaction of Eq. (4.9) which was evaluated earlier. The interactions of Eqs. (4.9) and (7.2) give a contribution which is the same to an order of magnitude to the transition probability for $E \sim w$.

The inverse relaxation time

$$\tau^{-1} = \frac{1}{12\pi}\xi^2\frac{ME^4}{\rho\hbar^4}\left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right), \tag{7.5}$$

can be determined by using Eq. (7.3) characterizing the relaxation in the level populations of a harmonic oscillator [Eq. (7.1)] for interaction with phonons. It follows from Eq. (7.5) that the quasilocal harmonic modes are well defined, i.e., $\hbar/\tau E \ll 1$, when $(E/\hbar\omega_D)^3 \ll 1$.

The mean free path of high-frequency phonons with $\omega \gg w/\hbar$ (but $\omega \ll \omega_D$) produced by the interaction of Eq. (7.3) is independent of T, and taking Eq. (6.4) into account is

$$L_s^{-1} = \frac{\pi}{6}\langle\xi^2\rangle\frac{MG\eta_L^{1/2}\hbar^3}{\rho v_s w^3}\omega^4. \tag{7.6}$$

The $L_s(\omega)$ relation is the same as for Rayleigh scattering, $\propto \omega^{-4}$. However, in our case this is due to the quadratic dependence of the density of states on energy [Eq. (6.4)] of quasilocal harmonic modes, and in the sense of the derivation of Eq. (6.4) is valid to

$$\hbar\omega \lesssim \min\left\{w\left(\frac{\delta\eta}{\eta_L}\right)^{1/2}, \ w\frac{\delta t}{\eta_L^{1/2}}\right\},$$

where $\delta\eta$ and δt are the scales of the fall-off in the distributions $\Phi(\eta)$ and $F(t)$.

For $E < \hbar\omega_D$ and the actual values of the parameters in Eq. (7.6) the ratio of the phonon mean free path to L is much less than unity, i.e., phonons with less than the Debye frequency remain well defined excitations in relation to resonance scattering by quasilocal harmonic modes. The expressions for L_s^{-1} [Eqs. (7.6) and (5.7)] are of the same order of magnitude for $\hbar\omega \sim w \sim T$.

Equation (7.6) corresponds to inelastic resonance interaction of phonons with quasilocal vibrations. As well as these, it is also important to take account of elastic scattering of phonons by microscopic regions for which the local quasielastic constants k are appreciably less than the mean value $\langle k \rangle \sim M\omega_D^2$, while the local vibrations are far from resonance with phonons. Each such region is characterized by a scattering cross section[42]

$$\sigma(k) \sim R_0^2\left(\frac{\langle k\rangle - k}{\langle k\rangle}\right)^2\left(\frac{\omega}{\omega_D}\right)^4, \tag{7.7}$$

where R_0 is of the order of the characteristic interatomic distance. Equation (7.7) describes the usual Rayleigh scattering by fluctuations in force constants. The mean free path corresponding to this mechanism is determined by the relation

$$L^{-1}(\omega) \sim \sigma(0)N_0, \quad N_0 \sim \int_{-\infty}^{\infty} d\eta\int_{-\infty}^{\infty} dt\,\Phi(\eta)F(t). \tag{7.8}$$

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Here N_0 is the characteristic concentration of regions with $k < \langle k \rangle$. Because of the increase in the function $\Phi(\eta)$ with an increase in η (see Fig. 2), Rayleigh scattering [Eq. (7.8)] can be more effective than Eq. (7.6). As a result, the coefficient of ω^4 in the $L^{-1}(\omega)$ dependence is noticeably greater than in Eq. (7.6). Its magnitude is determined by the form of $\Phi(\eta)$ for $\eta \gg \eta_L$. According to rough estimates, taking account of Rayleigh scattering can lead to an increase in $L_s^{-1}(\omega)$ by two orders of magnitude compared with Eq. (7.6). Since Eqs. (7.6) and (7.8) have the same frequency dependences, it will be convenient in what follows to take Rayleigh scattering into account by introducing an appropriate dimensionless coefficient μ into Eq. (7.6).

The calculation of the thermal conductivity at high temperatures is an incomparably more complicated problem than at low temperature where the TLS model works. We are not aware of an analytical form for the phonon mean free path $L(\omega, T)$ for $\omega \sim w/\hbar$, i.e., for energies where both rearrangement of the spectrum [Eq. (2.1)] and the mechanism of interaction with phonons take place. However, being interested in orders of magnitude estimates and the form of the temperature dependence of the thermal conductivity $\varkappa(T)$, we can proceed in the following way. We divide into two the region of integration in Eq. (5.1): the low frequency region with $\omega < w/\hbar$ and the high-frequency with $\omega > w/\hbar$. We will use the expression for $L(\omega)$ in Eq. (5.7) for the first region, corresponding to scattering of phonons by the TLS, while in the second region we use Eq. (7.6) multipled by the coefficient μ; this now represents scattering by harmonic quasilocal modes and Rayleigh scattering. In accordance with this, we write

$$\varkappa(T) = \varkappa_1(T) + \varkappa_2(T).$$

The first region with $T \gg w$ gives a contribution

$$\varkappa_1(T) \approx \frac{1}{12\pi^3} \frac{\rho \eta_L^{\,1/2}}{\hbar^2 G}\left(\frac{v_l}{d_\perp^2} + 2\frac{v_l}{d_l^2}\right) T, \tag{7.9}$$

corresponding to heat transport by prethermal phonons $\hbar\omega < w$. The origin of the $\varkappa_1 \propto T$ relation lies in the fact that prethermal phonons are scattered by TLS with level population differences which decrease with increasing T proportionally with T^{-1}. The mean free path then grows linearly with increasing T [see Eq. (5.7) for $\hbar\omega \ll T$] and their contribution to the thermal conductivity varies in the same way. The contribution from the high-frequency region $\hbar\omega \sim T \gg w$ (from thermal phonons) is independent of temperature:

$$\varkappa_2 \approx \rho w^2 (\mu\pi^3\hbar^2\langle\xi^2\rangle M G \eta_L^{\,1/2})^{-1}(1/v_l + 2/v_t) \tag{7.10}$$

and is mainly determined by phonons with energy of the order of [5] w. For $T \sim w$ and $\mu \lesssim 10^2$, as should be expected, $\varkappa_1 \sim \varkappa_2$ and agree to order of magnitude with Eq. (5.9).

The linear increase in thermal conductivity with temperature, [Eq. (7.7)] for $T > w$, produced by the contribution of prethermal phonons, corresponds with experimental results. For example, it is observed in the temperature range 20–100 K in g-SiO_2 (Ref. 2). The departure from the linear law for $\varkappa(T)$ at higher temperatures $T > 100$ K may be associated with the growth in the role of anharmonic processes

for propagating low-frequency phonons with $\hbar\omega < w$ interacting with thermal phonons.[47,48]

The arguments advanced determined $\varkappa(T)$ in two limiting cases: $T \ll w$ and $T \gg w$. In the intermediate region $T \sim w$, resonance scattering of phonons by anharmonic oscillators [Eq. (2.1)] with interlevel gaps $E \sim w$ is important. These oscillators are realized for $|\eta| \sim t^2 \sim \eta_L$. As has been shown,[31] the density of states in the potential of Eq. (2.1) has a van Hove singularity at energies $E \sim w$. The function $E_{21}(\eta, t)$, where E_{21} is the first interlevel gap, has saddle points in the η, t plane which, as shown by a numerical calculation,[6] occur for $\eta = 0$, $t = \pm 1.89\eta_L^{1/2}$. The energy $E_{21} = 2.18w$ corresponds to them. The function $E_{31}(\eta, t)$, where E_{31} is the distance between the first and third levels, has also, apart from two saddle points at $\eta = 0$, $t = \pm 2.15\eta_L^{1/2}$ to which the energy $E_{31} = 5.27w$ corresponds, points of absolute minimum at $\eta = -3.95\eta_L$, $t = 0$ and $\eta = 7.9\eta_L$, $t = \pm 5.62\eta_L^{1/2}$. The energy $E_{31} = 3.65w$ corresponds to all of them. A logarithmic divergence of the density of states corresponds to the saddle points and a finite jump in this quantity (from zero) to the points of absolute minimum. Only by using numerical methods can the effect of these features on the thermal conductivity be evaluated quantitatively. However, there is no doubt that the features of the density of states lead to an appreciable reduction in thermal conductivity $\varkappa(T)$ in a narrow temperature region. We consider that this effect is responsible for the existence of the more or less well marked plateau in the $\varkappa(T)$ relation observed in amorphous materials. It follows then from numerical values of the energies at which the van Hove singularities occurs that both the position of the plateau and its extent must be of the order of w. This prediction agrees with experimental results.[2]

§8. CONCLUSIONS

We have shown that within the framework of the approach described it is possible to describe the temperature dependence $\varkappa(T)$ of the thermal conductivity of amorphous systems over a wide temperature range, practically up to $T \lesssim 100$ K. It is significant that at all T considered, the thermal conductivity is determined by one-phonon scattering processes (an alternative point of view is described in Ref. 49). The complicated form of this dependence is then due to the existence of different groups of phonon scatterers, each of which gives its contribution to $\varkappa(T)$. Within the framework of the theory described, all these scatteres are described in a unified way as quantized oscillations in critical (soft) atomic potentials.

We note that the form $\varkappa(T) \propto T^2$ could be explained on the traditional AHVP model[11,12] only for very low $T \lesssim 1$ K. However, even in this temperature region the AHVP interpretation was incomplete, in that the constant of the deformation potential, γ, which appears in it remained an empirical parameter, the high value of which (~ 1 ev) was not explained. In the model we have used, a deformation potential of such an order of magnitude arises naturally. Its large value is a consequence of the softness of the anharmonic potentials for which TLS are realized.

We emphasize that we can go beyond the limits of appli-

cability of the AHVP model within the framework of the ideas presented, and describe a whole range of phenomena which were not realizable for that model. Among their number we must count the deduction contained in the present work of the existence of two types of TLS interacting differently with phonons, the existence in amorphous systems of quasilocal harmonic oscillations, the existence of a universal characteristic energy $w(\sim 30$ K) in the spectrum of vibrational states, the explanation of thermal conductivity processes at $T > w$, the excess specific heat for $T \sim w$,[31] the features of Raman scattering of light,[50] and also the anomalous thermal expansion of glasses.[41] In addition, the ideas of soft atomic potentials leads to agreement with experiment in the picture of electronic properties of glassy semiconductors.[51,52]

We assume that the existence of soft (critical atomic potentials is a consequence of the excess volume per atom in the materials considered. Apart from the model concepts,[53] this point of view is confirmed by experimental results of the study of small noncentral ions in crystals. Spectroscopic results show that for these the characteristic energy gaps between the levels of isolated wells are of the order of w (see, for example, Ref. 54), which is evidence of the softness of the atomic potentials.[55]

We note that the free volume hypothesis applicable to the nature of TLS was first formulated by Cohen and Crest.[56] However, these authors assumed hat the free volume is realized in the form of isolated macroscopic inclusions, at the boundaries of which nonsingle-welled atomic potentials arise. Our point of view takes the excess free volume as dispersed more or less uniformly in the amorphous system and has only microscopic local fluctuations. This point of view agrees with the results of recent experiments,[57] in which the excess free volume in amorphous Ge was varied by the conditions of preparing the specimens. Two-level systems arose in appreciable quantities only in specimens with the lowest density. It was shown experimentally in other work[58] that TLS effects appear in amorphous Ge on introducing large concentrations of oxygen. The oxygen atoms have smaller dimensions than germanium atoms and on replacing the latter excess free volume is formed.

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