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Theory of low-temperature thermal expansion of glasses

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We have developed a theory of low-temperature thermal expansion of glasses explaining a number of existing experimental data. We assume that thermal expansion, like many other low-temperature properties of glasses, is determined by associated two-level systems (TLS's); this concept has been introduced to explain these properties by Anderson, Halperin, and Varma and by Phillips. Our theory is based on the Karpov-Klinger-Ignat'ev model of two-level systems in glasses. The deformation potential of the TLS's is calculated. We have shown that it consists of two parts: The larger part (of the order of 0.3 eV) is responsible for the observed transport properties of glasses; however, it does not contribute to the thermal expansion of glasses. The latter is caused by a relatively small second part of the deformation potential which is, within logarithmic accuracy, proportional to the TLS interlevel spacing E. This is why at low temperatures the coefficient of thermal expansion of glasses is approximately a linear function of the temperature. Its sign is determined by a microscopic structure of the TLS. We have calculated the Grüneisen parameter Γ. It appears to be of the order of $(\mathscr{E}_a/\hbar\omega_D)^{2/3}\simeq 100$, where $\mathscr{E}_a$ is an energy of the order of 30 eV and ω_D is the Debye frequency. Such large values of Γ are connected with the softness of local anharmonic potentials that produce the TLS's in glasses. Our principal result is the dependence of the coefficient of thermal expansion α on the time of experiment, τ_{expt}. It is shown that if $\alpha<0$, then after heating glass it is at first contracted and afterwards, after the time about 10^{-8} sec (at $T=0.3$ K), a slow expansion begins. At $\tau_{\text{expt}}\simeq 1$ sec the parameter Γ can have the absolute value of about $\frac{1}{3}$ of that at $\tau_{\text{expt}}\simeq 10^{-8}$ sec. Such behavior of the thermal expansion coefficient is due to the fact that the contribution of the TLS's with large relative tunnel splitting ($\Delta_0/E\simeq 1$) is negative while that of the TLS's with small relative tunnel splitting ($\Delta_0/E\ll 1$) is positive. The latter, however, have large times of relaxation which can be comparable with the time of experiment. Finally, we discuss the relative role of the TLS's and free-electron contributions to the thermal expansion of metallic glasses.

I. INTRODUCTION

A number of low-temperature thermodynamical and transport properties of glasses can be understood within the framework of a phenomenological model of two-level systems (TLS's). This model has been introduced by Anderson, Halperin, and Varma[1] and Phillips.[2] According to the Anderson-Halperin-Varma-Phillips (AHVP) model, an atom or a group of atoms is associated with a TLS which resides in a double-well potential $V(x)$ in regard to some generalized coordinate x (see Fig. 1).

We suppose that the spacing between the two lowest levels E (Ref. 3) of such a system is much smaller than the distance to the third level. In such a case we have a two-level system with

$$E=(\Delta^2+\Delta_0^2)^{1/2}\,, \tag{1.1}$$

$\Delta_0=\hbar\omega_0\exp(-\lambda)$ being the tunneling parameter of the two-level system, while Δ describes the asymmetry of the potential $V(x)$ or, more exactly, the difference between the level positions in the two potential wells without regard to the tunneling. Here, ω_0 is of the order of the vibrational frequency in a well. The asymmetry Δ and the overlap parameter λ are supposed to be randomly and uniformly distributed over comparatively wide intervals of their values so that the corresponding density of states $N(\lambda,\Delta)$ is constant:

$$N(\lambda,\Delta)=N_0\,. \tag{1.2}$$

The coupling of a TLS with strain ε is described in the AHVP model by a deformation potential

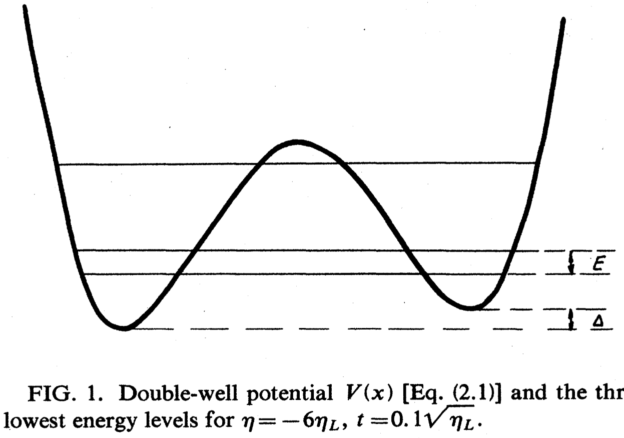

FIG. 1. Double-well potential $V(x)$ [Eq. (2.1)] and the three lowest energy levels for $\eta=-6\eta_L$, $t=0.1\sqrt{\eta_L}$.

$$\gamma = \frac{1}{2}\frac{\partial \Delta}{\partial \varepsilon} . \tag{1.3}$$

It is usually supposed to be uncorrelated with the TLS parameters Δ and Δ_0. Its value in glasses is of the order of 1 eV.

The AHVP model appeared to be very productive. On this basis, a number of low-temperature physical properties of dielectric and metallic glasses have been understood,[4–6] such as heat capacity, thermal conductivity, sound absorption and sound velocity variation with temperature, microwave absorption, phonon echo, etc. Properties of a number of other kinds of disordered systems, such as polymers,[7–9] superionic conductors,[10–12] neutron-irradiated quartz,[13–16] crystals with point defects,[17–19] etc., were explained on the basis of the AHVP model (see also Ref. 20). At the same time extremely interesting experiments on the thermal expansion of glasses[21–27] resulted in no explanation on the basis of this model.

A thermodynamical calculation gives the following equation for the coefficient of thermal expansion:

$$\alpha = \frac{1}{V}\left[\frac{\partial V}{\partial T}\right]_P = -\frac{1}{V}\left[\frac{\partial S}{\partial P}\right]_T . \tag{1.4}$$

Here, V is the volume of the glass, P is the hydrostatic pressure, and S is the entropy. It is natural to assume that at sufficiently low temperatures (roughly, below 1 K) thermal expansion is mainly due to the TLS contribution. For this contribution one can easily obtain the following equation (Phillips[28]):

$$\alpha = -\frac{1}{K}\sum_{\mathrm{TLS}} \frac{E}{4k_BT^2\cosh^2(E/2k_BT)}\frac{\partial E}{\partial \varepsilon} , \tag{1.5}$$

where k_B is the Boltzmann constant,

$$\frac{1}{K} = -\frac{1}{V}\left[\frac{\partial V}{\partial P}\right]_T \tag{1.6}$$

is the compressibility, and ε is the dilatation. The summation in Eq. (1.5) is over all of the TLS's in the unit volume of the nondeformed glass and we assume that their number depends on neither the pressure applied nor the temperature T.

For the derivative $\partial E/\partial \varepsilon$, which is by definition the deformation potential D, we have

$$D = \frac{\partial E}{\partial \varepsilon} = 2\frac{\Delta}{E}\gamma . \tag{1.7}$$

Combining Eq. (1.7) with (1.5) and (1.2), one gets the temperature-independent coefficient of thermal expansion α. However, by experiment at sufficiently low temperatures, α is almost a linear function of T,[26] so that one has approximately the Grüneisen relation

$$\Gamma = \frac{K\alpha}{C} = \mathrm{const} , \tag{1.8}$$

where C is the specific heat and Γ is the Grüneisen parameter. For a number of glasses it is only weakly dependent on temperature. Moreover, it has the two following unusual properties that need theoretical explanation: (1) as a rule, Γ is negative, and (2) the absolute values of Γ are very large, i.e., of the order of 10^2.

In solids whose thermodynamics is determined by phonons the Grüneisen relation is a direct consequence of the fact that the phonon-frequency variation with strain is proportional to the frequency itself, $-\Gamma$ being the coefficient of proportionality of the order of unity. The theory based on Eq. (1.5) would yield immediately the Grüneisen relation if one postulated proportionality between the deformation potential constant D and the TLS interlevel spacing E. However, such proportionality seems to be in contradiction with experimental data, especially those concerning ultrasonic absorption in glasses.[4] Indeed, the relaxational absorption coefficient l_{rel}^{-1} at low temperatures is proportional to T^3, while the assumption that γ is proportional to E would give the dependence $l_{\mathrm{rel}}^{-1} \sim T^7$ (for $l_{\mathrm{rel}}^{-1} \sim \gamma^4$).

In order to resolve this contradiction Ackerman *et al.*[26] supposed that different TLS's with the same value of interlevel spacing E might have deformation potentials D of opposite signs, so that the difference of TLS concentrations with given values of E and $|D|$, but opposite signs of D, is itself proportional to E. This implies the existence of some sort of correlation between the interlevel spacing E and the sign of deformation potential D.

Bartell and Hunklinger in their paper[29] where they studied ultrasonic absorption in amorphous SiO_2 under hydrostatic pressure also suggested that the deformation potentials of different TLS's might have opposite signs. These experiments show that the density of states of the TLS's per unit interval of E is practically independent of the pressure applied. Such independence was observed up to pressures of 4 kbar. Variation of interlevel spacing of the TLS at such pressures is of the order of 100 K (provided that γ is of the order of 1 eV), which exceeds by orders of magnitude the energies of those TLS's that are responsible for ultrasonic absorption at low temperatures. Therefore, the authors[29] came to the conclusion that there are approximately equal numbers of the TLS's with positive and negative γ.

The assumption that there are TLS's with both signs of deformation potential in glasses is quite natural. It does not alter the interpretation of the experiments on such transport phenomena as thermal conductivity, ultrasonic absorption, microwave absorption, etc., that are determined by the deformation potential squared. However, the second part of the hypothesis discussed in Ref. 26 introducing a correlation between the quantities D and E does not follow from the AHVP model and seems to be somewhat less natural. More precisely, it is not clear what physical reason results in a proportional to E predominance of the TLS's with a definite sign of deformation potential D.

To develop a theory of thermal expansion of glasses at low temperatures one should use a model where the correlation between the deformation potential and other parameters of a TLS emerges in a natural way. Such a theory should give the Grüneisen relation (1.8), i.e., approximately linear dependence of α on temperature, and explain large absolute values of the Grüneisen parameter.

To develop such a theory we shall exploit a model of a

TLS worked out by Karpov, Klinger, and Ignat'ev[30–32] (the KKI model). We shall see that this model, being equivalent to the AHVP model in other respects, permits one to obtain the Grüneisen relation (1.8) and accounts for the large observed values of the Grüneisen coefficient. Our calculations within the framework of the KKI model amount to calculation of the deformation potential $D=\partial E/\partial\varepsilon$ and subsequent summation of the contributions of the TLS according to Eq. (1.5). These results have been briefly reported in Ref. 33.

II. THE KKI MODEL

According to the model, the two-level systems are described by the anharmonic oscillator potential

$$V(x)=\mathscr{E}_a[\eta(x/a)^2+t(x/a)^3+(x/a)^4] \ . \tag{2.1}$$

Here, x is the generalized coordinate having the units of length and describing the motion of the tunneling entity, a is the characteristic length of the order of the interatomic spacing ($a\simeq 1$ Å), and $\mathscr{E}_a$ is the atomic energy of the order of $\overline{M}s^2=30$ eV, $\overline{M}$ and s being the average mass of atoms constituting the glass and the sound velocity, respectively. The values of the dimensionless parameters η and t are independent and random. Their distribution functions are schematically depicted in Figs. 2(a) and 2(b). The distribution of t is even because on the average a glass has a center of symmetry,[34] while the distribution of η reflects the hypothesis introduced in Refs. 30–32 concerning the existence of the so-called soft potentials in amorphous media. These are quasilocal and, in general, anharmonic modes with small and maybe negative values of the local quasielastic constants. These soft modes correspond to the tail of η distribution at $|\eta|\ll 1$ and are due to fluctuations of the structural parameters of a glass. It is possible to confine oneself to three terms of expansion of $V(x)$ because the ratio x/a is small for the typical values of the parameters η and t [see Eq. (2.5)]. In the end such a possibility is due to the softness of the potential $V(x)$.

The spectrum of the potential $V(x)$ is determined by the Schrödinger equation for an anharmonic oscillator

$$-\frac{\hbar^2}{2M}\frac{d^2\psi}{dx^2}+V(x)\psi=E_n\psi \ . \tag{2.2}$$

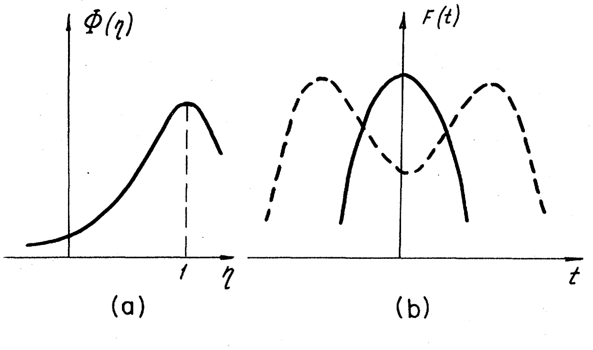

FIG. 2. Distribution functions of parameters η and t. The alternative possibility for the form of $F(t)$ is depicted by the dashed line.

Here, M is the mass of the tunneling entity which for estimating purposes we shall set to be equal to the average atom mass $\overline{M}$.

The scale of characteristic energies and displacements of the anharmonic oscillator was found in Ref. 31. It is given by the solution of the Schrödinger equation (2.2) (for the lowest eigenvalue) with discarded small terms proportional to η and t. For the potential $V=\mathscr{E}_a(x/a)^4$ the scale of characteristic energies is

$$W=\frac{\hbar^{4/3}\mathscr{E}_a^{1/3}}{2^{2/3}M^{2/3}a^{4/3}} \ , \tag{2.3}$$

while the characteristic displacement x/a is $\eta_L^{1/2}$, where

$$\eta_L=(\hbar^2/2Ma^2\mathscr{E}_a)^{1/3} \ . \tag{2.4}$$

The order-of-magnitude estimate for η_L is

$$\eta_L\simeq(\hbar\omega_D/\mathscr{E}_a)^{2/3}\simeq 10^{-2} \ ,$$

where ω_D is the Debye phonon frequency. For estimating purposes we assume $Ma^2\omega_D^2\simeq\mathscr{E}_a\simeq 30$ eV and $\hbar\omega_D/k_B\simeq 300$ K. The characteristic energy W is of the order of $\hbar\omega_D\eta_L^{1/2}\simeq 30$ K.

Now we introduce the dimensionless variables

$$\tilde{x}=\frac{x}{a\eta_L^{1/2}}, \quad \tilde{\eta}=\frac{\eta}{\eta_L}, \quad \tilde{t}=\frac{t}{\eta_L^{1/2}} \ . \tag{2.5}$$

These formulas reflect the fact that the scales of variation of the parameters η and t for the TLS's are η_L and $\eta_L^{1/2}$, respectively. In the new variables Eq. (2.2) turns into

$$-\frac{d^2\tilde{\psi}}{d\tilde{x}^2}+\tilde{V}(\tilde{x})\tilde{\psi}=\tilde{E}_n\tilde{\psi} \ , \tag{2.6}$$

where $\tilde{V}(\tilde{x})=\tilde{\eta}\tilde{x}^2+\tilde{t}\tilde{x}^3+\tilde{x}^4$ is the potential in the new coordinate $\tilde{x}$. It is dimensionless and differs from the initial potential by the factor $1/W$. The eigenvalues $\tilde{E}_n$ are related to the eigenvalues E_n by the equation

$$E_n=W\tilde{E}_n \ . \tag{2.7}$$

Thus, the characteristic energy scale for the potential (2.1) is $W\simeq 30$ K and characteristic atomic displacements are of the order of $x/a\simeq\eta_L^{1/2}\simeq 0.1$. Following the paper[31] we shall assume that the characteristic scales of variation of the distribution functions $\Phi(\eta)$ and $F(t)$ for the parameters η and t are bigger than η_L and $\eta_L^{1/2}$, respectively, so that in the regions of η and t variation in which we are interested, these functions can be considered as constants, independent of η and t.

At $t=0$ and $\eta<0$ the function $V(x)$ corresponds to symmetric double-well potential with the height of the barrier $V_0=W\tilde{\eta}^2/4$ and the distance between the minima $a(2|\eta|)^{1/2}$. The interlevel spacing between the two lowest levels is at $|\tilde{\eta}|\gg 1$:

$$\Delta_0=W\exp\left[-\frac{2^{1/2}}{3}|\tilde{\eta}|^{3/2}\right] \ . \tag{2.8}$$

This formula describes adequately the behavior of the function $\ln(W/\Delta_0)$ at $|\tilde{\eta}|\gg 1$. We shall see that this approach is sufficient to obtain all the results in the leading approximation in $\ln^{-1}(W/T)$, which is considered as a small parameter of the theory. As for the calculation of Δ_0 itself, the accuracy of Eq. (2.8) is insufficient because the terms of higher order in $|\tilde{\eta}|^{-1}$ make a significant contribution to the exponent in (2.8). Indeed, for instance, for $\tilde{\eta}=-6$, Eq. (2.8) gives $\Delta_0/W \simeq 10^{-3}$, while numerical solution of the Schrödinger equation[35] gives $\Delta_0/W=0.04$ (which is approximately equivalent to the tunnel splitting Δ_0 of 1 K). Under these conditions the distance to the third level is of the order of $100\Delta_0$, which gives some idea of the accuracy of the two-level model. Thus, according to the KKI model the TLS concept in glasses can be adequate only for energies E much smaller than $W \simeq 30$ K.

If $t \neq 0$ and $\eta < 0$, $|\tilde{\eta}| \gg 1$ and the potential $V(x)$ still remains a double-well potential, the condition of its weak asymmetry being $|\tilde{t}| \ll |\tilde{\eta}|^{-3/2}$. The energy spacing between the bottoms of the wells in this case is $\delta V = 2^{-1/2} W |\tilde{t}|\, |\tilde{\eta}|^{3/2}$. The spacing between the levels in two isolated wells (the asymmetry Δ) coincides with δV in the leading approximation. Thus,

$$\Delta = 2^{-1/2} W |\tilde{t}|\, |\tilde{\eta}|^{3/2} . \tag{2.9}$$

One can show that in general there are several points in the t-η plane that correspond to potential $V(x)$ of the same form. Their coordinates are connected by the transformation (see Karpov and Parshin[36])

$$\begin{aligned} \eta' &= \tfrac{1}{16}[9t^2 - 32\eta - 3t(9t^2-32\eta)^{1/2}] , \\ t' &= \tfrac{1}{2}[(9t^2-32\eta)^{1/2} - t] . \end{aligned} \tag{2.10}$$

In particular, if one of these points, say, A' belongs to the line $t=0, \eta<0$, two other points A belong to the parabola $\eta = t^2/4$ (see Fig. 3). The point A' with coordinates $0, \eta$ transforms into the point A with coordinates $(\sqrt{-8\eta}, -2\eta)$. According to Eq. (2.8) at $|\tilde{t}| \gg 1$, the tunnel splitting is

$$\Delta_0 = W \exp(-\tfrac{1}{48} |\tilde{t}|^3) . \tag{2.11}$$

Moreover, if point A is in the vicinity of the parabola $\eta = t^2/4$, it corresponds to a weakly asymmetric double-well potential with

$$\tilde{t}' = -8\tilde{R}/\tilde{t}, \quad \tilde{R} = \tilde{\eta} - \tilde{t}^2/4, \quad |\tilde{R}| \ll 1/\tilde{t}^2 . \tag{2.12}$$

Here, the parameter R describes the asymmetry for these TLS's.

If $|\tilde{R}| \ll 1/\tilde{t}^2$, $\tilde{\eta}'$ is determined by the same relation $\tilde{\eta}' = -\tilde{t}^2/8$ as before. Therefore, the asymmetry Δ is for this case [see Eq. (2.10)]

$$\Delta = \tfrac{1}{4} W |\tilde{R}|\, \tilde{t}^2 . \tag{2.13}$$

The TLS's that belong to the vicinity of the line $t=0$, $\eta<0$ we shall call the TLS's of the first type while those that belong to the vicinity of the parabola $\eta = t^2/4$ will be called the TLS's of the second type.[37] For both types the TLS's energy E is given by Eq. (1.1) where Δ_0 and Δ are determined by formulas (2.8) and (2.9), or (2.11) and (2.13) for TLS's of the first or second type, respectively.

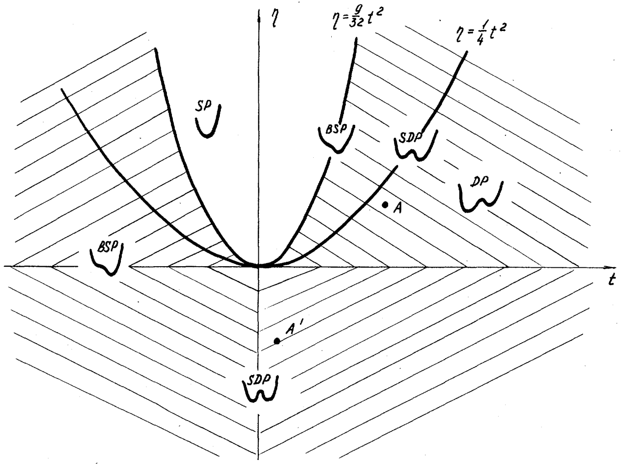

FIG. 3. The η-t plane. Solid lines discriminate between regions with a different form of the potential $V(x)$. SP is the single-well potential, DP is the double-well potential, SDP is the symmetric double-well potential, BSP is the single-well potential with bending. The points A and A' correspond to the potential $V(x)$ of the same form.

III. TLS—PHONON INTERACTION

Our task is to formulate the Hamiltonian of TLS's with regard to the slow varying in time of the deformation ε. It is natural to assume that in the presence of ε the coefficients η and t of the Hamiltonian (2.1) acquire additional contributions. In the linear approximation these contributions are proportional to ε: $\eta \to \eta + A_\eta \varepsilon$, $t \to t + A_t \varepsilon$. A question arises as to whether there is any correlation between A_η and A_t on the one side and the TLS parameters E and Δ_0 on the other. Such a correlation, if it existed, would strongly influence the general behavior of the thermal-expansion coefficient α, as can be seen from Eq. (1.5) and will be shown in more detail below. It will be apparent that A_η and A_t depend on the parameters η and t, and inasmuch as E and Δ_0 also depend on η and t, this dependence is a source of the aforementioned correlation.

To describe what we believe to be the main source of such a correlation let us recall that the potential $V(x)$ describes the "slow" motion of the tunneling entities with characteristic frequencies $\simeq W/\hbar$. Thus, $V(x)$ has a physical meaning of a potential averaged over the high-frequency vibrations of atoms of the glass (their frequencies being of the order of the Debye frequency ω_D). In the temperature interval $k_B T \lesssim W$ the high-frequency Debye modes are not excited; therefore, it is the temperature-independent interaction with the zero-point vibrations[38] that we will discuss here.

So far it has been sufficient to consider this interaction implicitly for it was natural to formulate the theory in terms of renormalized coefficients η and t. However, to evaluate the relation between A_η, A_t and the TLS parameters one should take into account such interaction explicitly. We begin with an analysis of the role of the interaction for $\varepsilon = 0$; the case of nonvanishing deformation will be considered below.

Let us start with the "bare" Hamiltonian describing an anharmonic oscillator (with the parameters η_0 and t_0 interacting with the high-frequency Debye modes Q_i). We need not consider harmonic terms of the form xQ_i because we assume x as well as Q_i to be normal modes and the harmonic part of the potential energy to have been diagonalized. The main anharmonic contribution is due to the cubic anharmonicity. Taking it into account we can write the interaction term in the form

$$b\mathcal{E}_a(x/a)\sum_i (Q_i/a)^2 \ , \tag{3.1}$$

b being a dimensionless constant of the order of unity.[39] As is well known (see, for instance, Ref. 40) the average of the sum is of the order of $\hbar\omega_D/\mathcal{E}_a$. Thus, after averaging we get an additional term to the oscillator potential of the form

$$\chi\mathcal{E}_a\eta_L^{3/2}x/a \ , \tag{3.2}$$

where χ is another dimensionless constant of the order of unity.

The term is linear in x, i.e., it describes a constant force acting upon the anharmonic oscillator. This force shifts the equilibrium position of the oscillator, the shift being equal to $\delta a(\eta_L)^{1/2}$, where δ can be obtained by solving the equation

$$\chi+2\tilde{\eta}\delta-3\tilde{t}\delta^2+4\delta^3=0 \ . \tag{3.3}$$

Such a shift leads to the change of both the harmonic and anharmonic constants. In other words, the parameters η_0 and t_0 should be replaced by the renormalized parameters η and t that are present in Eq. (3.3) and are given by

$$\tilde{\eta}_0=\tilde{\eta}-3\tilde{t}\delta+6\delta^2 \ , \tag{3.4a}$$

$$\tilde{t}_0=\tilde{t}-4\delta \ . \tag{3.4b}$$

It is convenient to consider the "bare" parameters t_0, η_0, and δ as functions of the renormalized ones because it is natural to assume that the distribution functions depicted in Fig. 2 are those for the renormalized parameters rather than for the bare ones.[41]

As one can see from Eqs. (3.2)—(3.4), order-of-magnitude estimates show that the differences $|\tilde{\eta}-\tilde{\eta}_0|$ and $|\tilde{t}-\tilde{t}_0|$ do not exceed unity in the actual region of η and t variation. Thus, the renormalization does not ruin the softness of the potential.

One can see that for both the TLS's of the first and second types (at $|\tilde{\eta}|\gg 1$ and $|\tilde{t}|\gg 1$, respectively), the second item in Eq. (3.3) considerably exceeds the third and the fourth ones. In the approximation of interest the latter term can be discarded. Iterating Eq. (3.3) (the small parameter being $|\tilde{\eta}|^{-1}$), we get

$$\delta=-\frac{\chi}{2\tilde{\eta}}+\tfrac{3}{8}\chi^2\frac{\tilde{t}}{\tilde{\eta}^3} \ . \tag{3.5}$$

For TLS's of the first type the last equation can be used directly; for TLS's of the second type it should be expressed through parameters $\tilde{t}$ and $\tilde{R}=\tilde{\eta}-\tilde{t}^2/4(|\tilde{t}|\gg 1, |\tilde{R}|\ll\tilde{t}^{-2})$:

$$\delta=-2\chi\tilde{t}^{-2}+8\chi\tilde{R}\,\tilde{t}^{-4}+24\chi^2\tilde{t}^{-5}-288\chi^2\tilde{R}\,\tilde{t}^{-7} \ . \tag{3.6}$$

As we shall see, only the two last terms of Eq. (3.6) contribute to thermal expansion.

Now let us turn to the case of nonvanishing deformation ε, which we shall assume to be a normal mode. The contribution of cubic anharmonic interaction in the linear approximation in ε can be written in the form

$$c\mathcal{E}_a\left[\frac{x}{a}\right]^2\varepsilon \ , \tag{3.7}$$

where again c is a dimensionless constant of the order of unity. In contrast to the constant b (or χ) introduced above, the constant c, being a coefficient at the second power of x, has a nonvanishing average value. Moreover, it is the sign of this average that determines the sign of the thermal expansion of the glass.

It is necessary to note that within the framework of our approach we have to consider the coefficients b and c as uncorrelated with the parameters η and t. This is justified because such correlation if it existed would include the scale of variation of the parameters of the order of unity, while we have so far discussed the possible correlation with the parameters η and t on the scale of their variation η_L and $\eta_L^{1/2}$, respectively.

The term (3.7) is equivalent to variation $(c/\eta_L)\varepsilon$ of the dimensionless parameter $\tilde{\eta}$. However, this is not the only contribution. There is another one; The shift of the center of the oscillator, which we have just discussed, is now deformation dependent. Indeed, to obtain the position of the center one should eliminate the linear in the x term of the whole Hamiltonian, including the deformation-dependent part. Because of anharmonicity this results in deformation-dependent contributions to the both parameters η and t. These contributions have the same origin and therefore each of them depends on both the parameters η and t.

To obtain explicit expressions for these one should eliminate the linear in the x term, as above, and retain in the resulting equations the term linear in ε. As a result, one gets for the derivatives $\partial\tilde{\eta}/\partial\varepsilon$ and $\partial\tilde{t}/\partial\varepsilon$,

$$\left.\frac{\partial\tilde{\eta}}{\partial\varepsilon}\right|_{\varepsilon=0}=\frac{c}{\eta_L}-\frac{3c}{\eta_L}\frac{\tilde{t}\delta}{\tilde{\eta}} \ , \tag{3.8}$$

$$\left.\frac{\partial\tilde{t}}{\partial\varepsilon}\right|_{\varepsilon=0}=-\frac{4c}{\eta_L}\frac{\delta}{\tilde{\eta}} \ . \tag{3.9}$$

The first term in (3.8) is the direct contribution of the cubic anharmonic (3.7), the other terms are due to the change of the harmonic and anharmonic constants as a result of the deformation-dependent shift of the equilibrium point.

Again for TLS's of the first type one can use these equations directly, inserting for δ, Eq. (3.5). For TLS's of the second type we also need the derivative $\partial\tilde{R}/\partial\varepsilon$. Using the equation $\tilde{\eta}=\tilde{R}+\tilde{t}^2/4$, we get within the accepted accuracy

$$\left.\frac{\partial\tilde{R}}{\partial\varepsilon}\right|_{\varepsilon=0}=\frac{c}{\eta_L}\left[1-4\frac{\delta}{\tilde{t}}+\frac{16\tilde{R}\delta}{\tilde{t}^3}\right] , \tag{3.10}$$

δ being determined by Eq. (3.6). The derivative $\partial\tilde{t}/\partial\varepsilon$ is determined by Eq. (3.9) where one should insert δ from (3.5) and express all the quantities in terms of $\widetilde{R}$ and $\widetilde{t}$. As a result, we have

$$\frac{\partial\widetilde{t}}{\partial\varepsilon}=\frac{32c\chi}{\eta_L\widetilde{t}^{\,4}}\left[1-\frac{4\widetilde{R}}{\widetilde{t}^{\,2}}+192\chi\frac{\widetilde{R}}{\widetilde{t}^{\,5}}-\frac{12\chi}{\widetilde{t}^{\,3}}\right]. \tag{3.11}$$

Only the last term proportional to $\widetilde{t}^{\,-7}$ is important for the thermal expansion; it originates from the third term in Eq. (3.6).

IV. DEFORMATION POTENTIAL OF A TLS

The deformation potential $D=\partial E/\partial\varepsilon$ is determined as

$$D=\frac{\partial E}{\partial\varepsilon}=\frac{\Delta_0}{E}\frac{\partial\Delta_0}{\partial\varepsilon}+\frac{\Delta}{E}\frac{\partial\Delta}{\partial\varepsilon}. \tag{4.1}$$

To calculate it, one should make use of Eq. (2.8) or (2.11) and of Eq. (2.9) or (2.13) (that relate the parameters Δ,Δ_0 with η and t for the TLS of the first and the second type, respectively) as well as of Eqs. (3.8) and (3.9) for the derivatives $\partial\widetilde{\eta}/\partial\varepsilon$ and $\partial\widetilde{t}/\partial\varepsilon$. For the TLS of the first type we have

$$\frac{\partial\Delta_0}{\partial\varepsilon}=\frac{c}{\sqrt{2}}\frac{W}{\eta_L}|\widetilde{\eta}|^{1/2}\exp\left[-\frac{\sqrt{2}}{3}|\widetilde{\eta}|^{3/2}\right], \tag{4.2}$$

$$\frac{\partial\Delta}{\partial\varepsilon}=\frac{\sqrt{2}cW}{\eta_L\sqrt{|\widetilde{\eta}|}}\left[\chi\,\mathrm{sgn}t-\tfrac{3}{4}|\widetilde{\eta}\widetilde{t}|-\tfrac{3}{4}\chi^2\frac{|\widetilde{t}|}{\widetilde{\eta}^{\,2}}\right]. \tag{4.3}$$

The first term in (4.3) is the largest. It comes from the term $(\partial\Delta/\partial t)(\partial t/\partial\varepsilon)$ and gives the main contribution to the deformation potential γ of the TLS of the first type:

$$\gamma_1=\frac{1}{2}\frac{\partial\Delta}{\partial\varepsilon}=6^{-1/3}c\chi\frac{W}{\eta_L}\frac{\mathrm{sgn}t}{\ln^{1/3}(W/\Delta_0)}. \tag{4.4}$$

We believe that this is the deformation potential of the AHVP theory that determines a number of transport coefficients of glasses such as thermal conductivity, sound absorption, phonon echo, etc. These coefficients are determined by γ^2, thus, the oddness in t is immaterial. A rough order-of-magnitude estimate of γ is $W/\eta_L \simeq 0.3$ eV, which seems to be in accordance with the results of experimental study of thermal conductivity (see Refs. 4 and 5). However, the term given by Eq. (4.4) does not contribute to the thermal expansion for it is odd in t, while the distribution function $F(t)$, as we have assumed, is even [see Fig. 2(b)].

The second and the third terms in Eq. (4.3) have come from $(\partial\Delta/\partial\eta)(\partial\eta/\partial\varepsilon)$ and $(\partial\Delta/\partial t)(\partial t/\partial\varepsilon)$ [from the second term in Eq. (3.5) for $\partial t/\partial\varepsilon$], respectively. Both are estimated, as compared to the first one, as the small parameter $\Delta/W \ll 1$. However, being even functions of t, they contribute to the thermal expansion.

One may anticipate that it is needless to retain the third term as compared to the second one, for their ratio is proportional to the small parameter $|\widetilde{\eta}|^{-1}\sim\ln^{-2/3}(W/\Delta_0)$. Yet, for the reason we shall discuss below, the third term will also be retained.

As a result, using Eqs. (2.8) and (2.9), we get

$$D_1=\frac{cW}{\eta_L}\left[1.10(1-p)^{1/2}\frac{\mathrm{sgn}t}{L^{2/3}}+0.91\frac{E}{W}\left[pL^{1/3}-\frac{1-p}{L^{2/3}}\right]\right.$$
$$\left.-0.2\chi^2\frac{E}{W}\frac{1-p}{L^{8/3}}\right], \tag{4.5}$$

where we have introduced the notations

$$p=(\Delta_0/E)^2,\quad L=\ln(W/Ep^{1/2}). \tag{4.6}$$

Only the three last terms in Eq. (4.5) contribute to the thermal expansion.

In the same manner, making use of Eqs. (2.11), (2.13), (3.6), (3.9), and (3.10), we get for the TLS of the second type,

$$\frac{\partial\Delta_0}{\partial\varepsilon}=24c\chi^2(W/\eta_L)|\widetilde{t}|^{-5}\exp(-|\widetilde{t}|^3/48), \tag{4.7}$$

$$\frac{\partial\Delta}{\partial\varepsilon}=\frac{cW}{\eta_L}(\tfrac{1}{4}\widetilde{t}^{\,2}\mathrm{sgn}R+192\chi^2|\widetilde{R}|\widetilde{t}^{\,-6}). \tag{4.8}$$

In the temperature range of interest ($T \ll W$) the distribution functions $\Phi(\eta)$ and $F(t)$ of the random variables η and t can be considered as constants independent of η and t. This is a direct consequence of the assumption that $\Phi(\eta)$ and $F(t)$ can be considered as constants at least in the intervals of the order of η_L and $\eta_L^{1/2}$ of η and t variation, respectively, near the points $\eta=0$ and $t=0$. As $(\partial R/\partial\eta)_t=1$, the same is true for the distribution of the parameters t and R. This means, in particular, that the distribution functions are even functions of these parameters, and only even terms in the expression for the deformation potential D_2 can contribute to the thermal expansion. Only such terms are retained in Eqs. (4.7) and (4.8).

The first term in Eq. (4.8) is the exception. It is the largest term (by its absolute value) coming from $(\partial\Delta/\partial R)(\partial R/\partial\varepsilon)$. Being odd in R, it does not contribute to the thermal expansion. However, this is the deformation potential describing the contribution of the TLS of the second type to the transport phenomena. We have

$$\gamma_2=\frac{1}{2}\frac{\partial\Delta}{\partial\varepsilon}=(\tfrac{9}{2})^{1/3}c(W/\eta_L)\ln^{2/3}\left[\frac{W}{\Delta_0}\right]\mathrm{sgn}R. \tag{4.9}$$

The ratio of the main contributions to the deformation potentials of the TLS of the second and the first types is

$$\frac{\gamma_2}{\gamma_1}=\frac{3\ln(W/\Delta_0)}{\chi}. \tag{4.10}$$

If $W/\Delta_0=600$ (which corresponds to the tunnel splitting $\Delta_0=0.05$ K or $\Delta_0/2\pi\hbar=1$ GHz), the numerator in Eq. (4.10) is about 20. χ being of the order of unity, it is natural to conclude that the TLS's of the second type are coupled to phonons much stronger than the TLS's of the first type. This agrees with the concept introduced by Black and Halperin[42] that there are TLS's of two kinds in glasses, that interact with phonons in a different way.[43] The concept permits one to reconcile the fact that the values of deformation potential γ given by experiments with phonon echo are much bigger than those extracted from combined data on ultrasonic absorption and heat capacity.

Using (4.7) and (4.8) one can easily calculate the deformation potential for the TLS of the second type. Introducing the variables E and p, we get

$$D_2=\frac{cW}{\eta_L}\left[3.30(1-p)^{1/2}L^{2/3}\mathrm{sgn}\left[\eta-\frac{t^2}{4}\right]\right.$$
$$\left.+0.038\chi^2\frac{E}{W}\left[\frac{p}{L^{5/3}}+0.67\frac{1-p}{L^{8/3}}\right]\right] . \tag{4.11}$$

We see that Eqs. (4.5) and (4.11) for the deformation potentials of the TLS's of the first and the second types are quite different, although the potentials $V(x)$ for both cases may be identical. The point is that for the TLS of the second type the potential $V(x)$ can be a double-well one only because of an asymmetric environment, whereas for the TLS of the first type the potential can be a double-well one regardless of the environment. This is why strain acts upon the TLS's of the two kinds in a different way.

V. DENSITY OF STATES IN THE KKI MODEL: AVERAGING OVER TUNNEL PARAMETERS

To calculate the coefficient of thermal expansion α using Eq. (1.5) one should know the density of states $N_{1,2}(E,p)$ for the TLS's of the first and the second types as a function of E and p. Going from the variables η,t (for the first type) or from the variables t,R (for the second type) to the variables E,p we get

$$N_{1,2}=\tfrac{2}{3}(\tfrac{4}{3})^{1/3}\psi_{1,2}\eta_L^{3/2}W^{-1}p^{-1}(1-p)^{-1/2}L^{-4/3} , \tag{5.1}$$

where

$$\psi_j=\Phi(\eta_j)F(t_j) , \tag{5.2}$$

$j=1,2$, and the characteristic values of the parameters η_j and t_j are weakly (logarithmically) dependent on E and p [see (2.8), (2.9), (2.11), and (2.13)]. Therefore, ψ_j will be further considered as constants independent of E and p and thus as additional parameters of the theory.

We shall perform the integration in Eq. (1.5) with the weight (5.1) in two stages. At first we shall average over the tunnel parameter p, introducing an auxiliary quantity

$$Q_j(E)=\int_{p_0}^{1}D_jp^{-1}(1-p)^{-1/2}L^{-4/3}dp,\ j=1,2 . \tag{5.3}$$

The lowest limit p_0 corresponds to the smallest value of Δ_0/E. This value can be found from the following arguments. Equation (1.5) is a thermodynamical formula taking into account the contributions of those TLS's that are in thermal equilibrium with their environment. Roughly, these are the TLS's that had time to make at least one transition during the duration of the experiment, τ_{expt}. According to Ref. 6,

$$p_0=\tau_{\min}(E)/\tau_{\mathrm{expt}} , \tag{5.4}$$

where $\tau_{\min}(E)$ is the minimal value of the relaxation time of the TLS occupancy for a given value of E.

Inserting Eqs. (4.5) or (4.11) into (5.3) and performing the integration, we get

$$Q_1(E)=1.82\frac{cE}{\eta_L}\{\ln^{-1}[W/E(p_0)^{1/2}]$$
$$-0.07\chi^2\ln^{-3}(W/E)\} \tag{5.5}$$

for the TLS's of the first type and

$$Q_2(E)=0.09c\chi^2\eta_L^{-1}E\ln^{-3}(W/E) \tag{5.6}$$

for the TLS's of the second type.

It is readily seen from Eq. (5.5) why it appeared necessary to take into account a finite time of experiment while averaging over the tunnel parameter Δ_0. Although the first term in Eq. (5.5) vanishes at $\tau_{\mathrm{expt}}\to\infty$, it can still exceed the second one for finite τ_{expt} because the second term contains, in the denominator, a large logarithm in the third power. Note that the second term of Eq. (5.5) originates in the third term of Eq. (4.3). This is why we have not discarded it: at $\tau_{\mathrm{expt}}\to\infty$ there is a full compensation of the contributions into thermal-expansion coefficient from the variation of the tunnel parameter Δ_0 [Eq. (4.2)] and of the asymmetry Δ [Eq. (4.3), the second term] with deformation. The origin of such a compensation lies in the fact that on the one hand, within accepted accuracy, the distribution function ψ_1 is considered as a constant independent of η and t, and on the other hand, there is a contribution to $\partial\eta/\partial\epsilon$ for the TLS of the first type independent of the TLS parameters [the first term in Eq. (3.8)]. It can be shown that the corresponding contribution of the TLS's of the first type vanishes at $\tau_{\mathrm{expt}}\to\infty$, irrespective of the explicit form of the functional dependence of Δ and Δ_0 on η. For the TLS's of the second type such cancellation of the two terms at $\tau_{\mathrm{expt}}\to\infty$ does not take place and the terms depending on τ_{expt} have been discarded in comparison with the terms retained in Eq. (5.6).

VI. COEFFICIENT OF THERMAL EXPANSION: GRÜNEISEN RELATION

Making use of Eqs. (5.5) and (5.6) and performing an integration over E in Eq. (1.5), we obtain the contribution to the thermal-expansion coefficient from the TLS's of the first type:

$$\alpha^{(1)}=-\frac{2\pi^2}{9}\frac{c\psi_1\eta_L^{1/2}k_B^2T}{WK}\left[\left[\mathcal{L}+\tfrac{1}{2}\ln\frac{\tau_{\mathrm{expt}}}{\tau_{\min}(T)}\right]^{-1}\right.$$
$$\left.-0.07\chi^2\mathcal{L}^{-3}\right] , \tag{6.1}$$

where

$$\mathcal{L}=\ln(W/k_BT) ,$$

and from the TLS's of the second type,

$$\alpha^{(2)}=-0.11\frac{c\psi_2\eta_L^{1/2}k_B^2T}{WK}\chi^2\mathcal{L}^{-3} . \tag{6.2}$$

Both contributions are proportional to the temperature T and, in addition, have a weaker (logarithmic) temperature dependence. It is interesting to note that the $\tau_{\rm expt}$-independent contributions from the TLS's of the first and the second types have opposite signs.

For the heat capacity in the KKI model we have [see Ref. 31 and also Eq. (5.1)][44]

$$C_j=\tfrac{2}{3}(\tfrac{4}{3})^{1/3}\pi^2\psi_j\eta_L^{3/2}W^{-1}k_B^2T\mathscr{L}^{-1/3},\ \ j=1,2\ . \tag{6.3}$$

Inserting this equation, as well as (6.1) and (6.2) into Eq. (1.8), we get for the Grüneisen parameter,

$$\Gamma=-0.55c\eta_L^{-1}(1+\psi)^{-1}\mathscr{L}^{1/3}\left[\left[\mathscr{L}+0.5\ln\frac{\tau_{\rm expt}}{\tau_{\rm min}(T)}\right]^{-1}-0.037\chi^2(1-\tfrac{11}{16}\psi)\mathscr{L}^{-3}\right], \tag{6.4}$$

where $\psi=\psi_2/\psi_1$ is the ratio of the densities of the TLS's of the second and the first types. The first term in the square brackets is the $\tau_{\rm expt}$-dependent contribution to the Grüneisen parameter; it vanishes at $\tau_{\rm expt}\to\infty$. The second term is $\tau_{\rm expt}$ independent; its sign is determined by the ratio $\psi=\psi_2/\psi_1$.

The sign of the Grüneisen parameter, i.e., the sign of the thermal-expansion coefficient, is determined also by the sign of the numerical coefficient c describing the deformation-induced variation of the harmonic parameter η of the oscillator (2.1). The coefficient c in Eqs. (6.1), (6.2), and (6.4) should be understood as an average value of the coefficient introduced by Eq. (3.7). The inequality $c>0$ corresponds to the physical picture where under compression of the glass the parameter η diminishes. If prior to application of deformation its value is negative its absolute value enhances, i.e., the height of the tunnel barrier increases. One can see that the same is true for the TLS of the second type as well.

One can give the following qualitative explanation of the $\tau_{\rm expt}$ dependence of the Grüneisen parameter. The enhancement of $|\eta|$ for the TLS's of the first type under compression of the glass results (at $c>0$), on the one hand, in a decrease of the tunnel parameter Δ_0 [see Eq. (2.8)] and, on the other hand, in an increase of the asymmetry Δ [see Eq. (2.9)]. Therefore, the contributions to the thermal expansion from the TLS's of the first type with the almost symmetric double-well potentials ($\Delta<\Delta_0$) and with strongly asymmetric potentials ($\Delta\gg\Delta_0$) are of opposite sign and cancel each other exactly, provided $\partial\eta/\partial\varepsilon$ is independent of η and the distribution function ψ_1 is constant. In other words, there is a cancellation of the contributions of the first and the second terms in the square brackets in Eq. (4.5) originating in $\partial\Delta_0/\partial\varepsilon$ [Eq. (4.2)] and in $\partial\Delta/\partial\varepsilon$ [Eq. (4.3)], respectively. Namely, the TLS's of the first type with

$$[1+\ln(W/E\sqrt{p}\,)]^{-1}<p\le 1\ , \tag{6.5}$$

i.e., with relatively small barriers and small times of relaxation [of the order of $\tau_{\rm min}(E)$] at $c>0$, make negative contributions to the thermal-expansion coefficient. On the contrary, the TLS's of the first type with

$$p<[1+\ln(W/E\sqrt{p}\,)]^{-1}\ , \tag{6.6}$$

i.e., with large times of relaxation, make positive contributions to the thermal-expansion coefficient α and to the Grüneisen parameter Γ. Therefore, glass, after initial heating, at first contracts (provided $c>0$ and the contribution of the TLS's of the first type is predominant) and then begins to expand as the TLS's of the first type with larger times of relaxation are thermalized. The final result depends on the time of the experiment $\tau_{\rm expt}$ and on the ratio of the concentrations of the TLS's of the first and the second types (the parameter $16/11\psi$ as compared to 1).

Thus, for $\tau_{\rm min}(T)\simeq10^{-8}$ sec, which in dielectric glasses corresponds to a temperature of about 0.3 K and $\tau_{\rm expt}=1$ sec, we have $\ln[W/k_BT(p_0)^{1/2}]\simeq10$ and $\mathscr{L}^3\simeq40$. The resulting sign is determined by the constant χ in Eq. (6.4). If one uses the estimates based on the experimental data[4,45]

$$\gamma_2/\gamma_1\simeq5 \ \text{ for } E/2\pi\hbar\simeq1\ \text{GHz}\ ,$$

then one gets from (4.10) $\chi\simeq4$. On the other hand, it is known (see Ref. 42) that in glass the TLS's strongly coupled to the phonons have a much smaller concentration than those weakly coupled to the phonons. As a result, it appears that the second term in Eq. (6.4) is smaller than the first one by approximately a factor of 7. This means that for typical times of experiment the main contribution to the coefficient of thermal expansion is negative and, $\tau_{\rm expt}$ increasing, slowly decreases by the absolute value. For example, as $\tau_{\rm expt}$ increases from 1 sec up to 1 min, $|\Gamma|$ diminishes by about 20% of its initial value.

As it is seen from Eq. (6.4), the order of magnitude of the "constant" Γ is determined by the "adiabatic" parameter η_L and appears to be $\eta_L^{-1}\simeq100$. This agrees with the experimental data for the fused silica where $\Gamma\simeq-70$. The values of this order can be obtained from Eq. (6.4) setting $c=5$—7. Such large values are not surprising for the potential energy of the interaction of atoms in solids can usually be approximated by a function going as a large negative power of interatomic distance (e.g., the Lennard-Jones potentials), and the constants c and χ are proportional to the third derivative of this function.

VII. DISCUSSION AND CONCLUSIVE REMARKS

One of the most important predictions of our theory that permits direct experimental verification is a nonstationary behavior of the Grüneisen "constant" Γ. The logarithm in the denominator of the corresponding term in Eq. (6.4) is

$$\mathscr{L}+\tfrac{1}{2}\ln\left[\frac{\tau_{\text{expt}}}{\tau_0}\right],$$

where $\tau_0=\tau_{\min}(T)$. At $T\approx0.3$ K, τ_0 is about 10^{-8} sec. This means that two experiments where Γ is measured may give two values that differ by, for instance, 30% if one experiment is performed during a minute and the other during a day [we suppose that the first term in Eq. (6.4) is predominant].

On the other hand, it is the nonstationary part that should give large absolute values of the Grüneisen constant, for in the denominator of the corresponding equation there is a small parameter η_L. Of course, the same parameter is present also in the denominator of the second term of Eq. (6.4). However, there is also a large factor $\mathscr{L}^3$ so that the resulting product should by no means necessarily be small.

Observation of such nonstationary behavior of Γ would provide serious evidence of the correctness of both the KKI model and the estimation of the deformation potential based on the analysis of the zero-point vibrations. Moreover, it can appear that there exist several types of glasses. Glasses of one type may behave according to the KKI model while glasses of another type may be described by some other model. We think that it is very interesting to investigate the behavior of the thermal expansion in other models describing the low-temperature properties of glasses.

Another conclusion following from Eq. (6.4) is that the Grüneisen parameter Γ is slightly temperature dependent [see Eq. (6.4)]. If the temperature goes down, $|\Gamma|$ enhances, which is in qualitative agreement with the experimental data.[26]

Experimental investigation of the low-temperature thermal expansion of glasses can provide a number of important data concerning the TLS's. Analysis of the whole complex of experimental data on thermal expansion, heat capacity, thermal conductivity, phonon echo, and sound absorption would permit one to determine the ratio ψ of the densities of the TLS's of the first and the second types and their constants of deformation potential contributing to these phenomena (i.e., the parameters c and χ). Investigation of thermal expansion can permit one to determine the sign of the constant c, i.e., to make conclusions concerning variation of the tunnel barrier under the influence of deformation and thus to elucidate the problems concerning the microscopic structure of the TLS's and check the adequacy of various microscopic models.

Indeed, let the TLS's be a stretched linear three-atom system so that the middle atom is in a double-well potential. Contraction of such a three-atom system diminishes the height of the barrier, so that in this case $c<0$. If, on the other hand, the atomic configuration is not linear (angular configuration), contraction of the system may heighten the barrier, which would mean $c>0$. Phillips[5] was the first to point out that thermal expansion is sensitive to the microscopic structure of the TLS.

The results obtained above are based on the assumption of constancy of the distribution functions of the parameters η and t on the scale η_L and $\eta_L^{1/2}$, respectively. There are indications in the literature (see Ref. 46) that introduction of impurities in glass may violate the constancy. In such a case one may anticipate that the thermal expansion of glasses at low temperatures is more sensitive to the addition of impurities than, for example, such properties as heat capacity or thermal conductivity. Indeed, as we have seen, for the same value of energy E the TLS's of the first type with $\Delta_0\ll E$ make a positive contribution to thermal expansion while the contribution of the TLS's with $\Delta_0\simeq E$ is negative. We assume that in pure glasses the distribution functions of the parameters η and t are almost constant within the range of their variation of the order of η_L and $\eta_L^{1/2}$, respectively. As a result, both contributions almost cancel out each other.

If the introduction of impurities of a certain kind violates the constancy, thus bringing about predominance of the TLS with, say, a certain value of the tunnel parameter Δ_0, there will be no such compensation. This may be related to the experimental fact[26] that the thermal expansion of glasses is sensitive to the impurity contents.

Such sensitivity may be characteristic not only of thermal expansion but of some other properties of glasses too. For instance, if the peak in the Δ_0 distribution is sufficiently pronounced, the nonresonant ultrasonic absorption coefficient may go in the low-frequency limit as $\omega^{3/2}$ instead of the usual proportionality to the first power of the frequency ω.

Finally, let us discuss the thermal expansion of metallic glasses where conduction electrons provide an additional contribution to thermal expansion.[47] This contribution can be written as

$$\alpha^{(e)}=-\frac{1}{K}\int_0^\infty dE\,\nu(E)\frac{E-\mu}{4k_BT^2\cosh^2\left[\dfrac{E-\mu}{2k_BT}\right]}\Lambda(E)\,. \tag{7.1}$$

Here, $\nu(E)$ is the density of the electron states as a function of the electron energy E, μ is the electron chemical potential, and $\Lambda(E)$ is the electron deformation potential averaged over the electron states with the same energy E. Expanding the deformation potential near the Fermi level, we have

$$\Lambda(E)=\Lambda'(E-\mu)\,. \tag{7.2}$$

Here, we have taken into account that $\Lambda(\mu)=0$: this is the electric neutrality condition (see Ref. 48). As a result, we get for the electron contribution to the thermal-expansion coefficient,

$$\alpha^{(e)}=-\frac{\pi^2}{3}\frac{\nu(\mu)\Lambda' k_B^2T}{K}\,. \tag{7.3}$$

For the free-electron model, $\Lambda'=-\frac{2}{3}$ (see Ref. 48) and

$$\alpha^{(e)}=\frac{2\pi^2}{9}\frac{\nu(\mu)k_B^2T}{K}\,. \tag{7.4}$$

$\alpha^{(e)}$ is proportional to the temperature T and is positive. Let us compare the contributions from the free electrons and the TLS's. We have

$$\frac{\alpha^{(e)}}{|\alpha^{(\mathrm{TLS})}|} \simeq \frac{\nu(\mu)\eta_L}{N_0} . \tag{7.5}$$

Here, N_0 is the density of the TLS's states: $N_0 \simeq \psi_1 \eta_L^{3/2}/W \simeq 10^{33}$ erg^{-1} cm^{-3}. Inasmuch as for typical metals $\nu(\mu) \simeq 10^{35}$ erg^{-1} cm^{-3} and $\eta_L \simeq 10^{-2}$, the ratio (7.5) is of the order of unity. This may provide an explanation for the fact that the coefficients of thermal expansion for a number of metallic glasses are positive and have the same order of magnitude as for dielectric glasses.[26]

We think that to check the hypothesis we have just formulated, it would be very interesting to investigate experimentally the thermal expansion of metallic glasses in the superconducting state. At $T < T_c$ (T_c being the temperature of the superconducting transition) the electron contribution to α would decrease with temperature exponentially and what remained would be the TLS contribution. If this surmise is correct and the TLS in dielectric and metallic glasses are similar, one might expect an essential change of α in the temperature interval near T_c and even the change of its sign.

Finally, let us emphasize once more that, in our opinion, large absolute values of the Grüneisen parameter in glasses are directly connected with the softness of the local anharmonic potentials that produce the TLS. A similar picture will probably be found in crystals with tunnel defects,[49] and to analyze thermal expansion of such crystals an analogous approach may prove fruitful.

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[38] Karpov and Parshin were the first to point out that for adequate description of the TLS-phonon interaction it is necessary to take into account the high-frequency zero-point vibrations. See V. G. Karpov, and D. A. Parshin, Zh. Eksp. Teor. Fiz. **88**, 2212 (1985) [Sov. Phys.—JETP (to be published)].

[39] Within the framework of the physical picture described, b should be considered as a random quantity with equal probabilities for the values b and $-b$, so that its average vanishes. Its modulus is centered at a certain value of the order of unity.

[40] V. L. Gurevich, *Kinetics of Phonon Systems* (Nauka, Moscow, 1980) (in Russian).

[41] One can show that this assumption is not critical. If the distribution function was constant in the variables η_0 and t_0, it would change Eqs. (4.5) and (4.11) only insignificantly, affecting only numerical coefficients of the last terms in each.

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[43] Similar observation has also been made in Ref. 31.

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