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TEMPERATURE DEPENDENCE OF GRÜNEISEN'S PARAMETERS IN A SOLID WITH POLYATOMIC BASIS

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The temperature dependence of Grüneisen's parameters $\gamma^{ac}\left(\frac{\Theta_D}{T}\right)$ and $\gamma^{op}\left(\frac{\Theta_E}{T}\right)$ for acoustic and optical lattice vibrations, as part of total Grüneisen's parameter in a solid with polyatomic basis is analysed in the frame of the Debye-Einstein approximation. The results are obtained using Debye's $\Theta_D(T)$ and Einstein's $\Theta_E(T)$ temperatures and the separated theoretical and experimental contributions of the isochoric specific heats $C_V^{ac}(T)$ and $C_V^{op}(T)$ for acoustic and optical vibrations, respectively. Both Grüneisen's parameters decrease with the temperature and this behaviour is discussed in the frame of competition between the temperature dependence of vibrational frequencies due to volume change and lattice anharmonicity effects. There are compared the theoretical curves and experimental curves in the case of undoped bismuth silicon oxyde ($Bi_{12}SiO_{20}$) crystal.

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1. Introduction

Introduced many decades ago to describe some thermodynamic coefficients (adiabatic and isothermal compressibility, thermal expansion, specific heats and others) Grüneisen's parameter is still of interest being treated in various theoretical and experimental papers or monographs [1-6]. During the time, various physical problems have been connected to mean Grüneisen's parameter defined by

$$\gamma = \frac{\sum_i \gamma_i C_i}{\sum_i C_i} \tag{1}$$

where $\gamma_i = -\frac{d\ln\omega_i}{d\ln V}$ is thermal Grüneisen's parameter for an individual excited lattice mode $i = \vec{q}\lambda$ ($\vec{q}$ is the wave vector and λ is the polarization branche of the i-th vibrational frequency ω_i), C_i is the specific heat of i-th vibration mode and V is the crystal volume. Thus, the mean Grüneisen's parameter γ, referred in this paper as Grüneisen's parameter, is consistent with the quasiharmonic approximation [1] being connected with the isochoric thermal expansion coefficient α_V, the bulk modulus B_T and the specific heat C_V (or isobaric corresponding coefficients).

It is well-known that a temperature increase alters the equilibrium volume due to the thermal expansion and simultaneously increases the vibrational amplitudes of the atoms about their equilibrium positions. The effect on the frequency of a change in the temperature T, at constant pressure P, is thus described by $\left(\frac{\partial\omega}{\partial T}\right)_P = \left(\frac{\partial\omega}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial\omega}{\partial T}\right)_V$, where the first term giving the

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"implicit" contribution accounts for the volume driven frequency changes due to thermal expansion and the second one the "explicit" contribution accounts for the changes in the vibrational amplitudes, and thus for the phonon-population driven anharmonic frequency shifts at constant volume [7]. Some thermodynamic properties as the thermal state equation, the isobaric specific heat $C_P(T)$ and the linear expansion coefficient $\alpha_P(T)$ of a solid with polyatomic basis have been analysed theoretically in the frame of the Debye-Einstein approximation, taking into account simultaneously, the contributions of acoustic and optical vibrations [7,8]. The theoretical difference $C_P - C_V = 3C_V\alpha_P\gamma T$ between the isobaric and the isochoric heats has depends on the parameters: Debye's Θ_D, Einstein's Θ_E temperatures and Grüneisen's γ^{ac} and γ^{op} parameters. However, because the experimental data give $C_{P,ex}(T)$, a comparison with the theoretical results implies often to know the separate contributions of the experimental isochoric specific heats $C_{V,ex}^{ac}(T)$ and $C_{V,ex}^{op}(T)$. This problem has been analysed in [9] for the case of undoped $Bi_{12}SiO_{20}$, (a crystal with polyatomic basis) in the frame of the Debye-Einstein approximation, considering that both Debye's Θ_D and Einstein's Θ_E temperatures depend themselves of the temperature T. In fact, this means that implicitly the vibrational anharmonicity has been taken into account in a semi-empirical way through $\alpha_P(T)$ and $\gamma(T)$.

The purpose of this work is to study the temperature dependence of acoustic, optical $\gamma^{op}\left(\frac{\Theta_E}{T}\right)$ and total $\gamma\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right)$ Grüneisen's parameters obtained in the Debye-Einstein approximation for a solid with polyatomic basis using Debe's $\Theta_D(T)$ and Einstein's $\Theta_E(T)$ temperatures and the separate theoretical and experimental contributions of the isochoric specific heats $C_{V,ex}^{ac}(T)$ and $C_{V,ex}^{op}(T)$, respectively. The paper discusses the influence of the vibrational anharmonicity on the Grüneisen's parameters in the case of undoped $Bi_{12}SiO_{20}$ crystal in the temperatures range between $300\,K$ and $900\,K$.

2. Theoretical

For a normal vibration mode $i = \vec{q}\lambda$ the dispersion law in the Debye approximation is given by $\omega_{\vec{q}s} = v_{s\lambda}(\theta_{\vec{q}}, \varphi_{\vec{q}})q$, where $v_{s\lambda}(\theta_{\vec{q}}, \varphi_{\vec{q}})$ for $\lambda = 1,2,3$ is the sound velocity, whereas in the Einstein approximation $\omega_{\vec{q}s} = \omega_{0\lambda} = \omega_E$ for $\lambda = 4,5,...3s$, where s is the number of atoms in the elementary cell. In agreement with the relation (1) the total Grüneisen's parameter of the crystal with polyatomic basis may be expressed by

$$\gamma = \frac{\sum_{\lambda=1}^{3}\sum_{\vec{q}}\gamma_{\vec{q}\lambda}^{ac}C_{V,\vec{q}\lambda}^{ac} + \sum_{\lambda=4}^{3s}\sum_{\vec{q}}\gamma_{\vec{q}\lambda}^{op}C_{V,\vec{q}\lambda}^{op}}{\sum_{\lambda=1}^{3}\sum_{\vec{q}}C_{V,\vec{q}\lambda}^{ac} + \sum_{\lambda=4}^{3s}\sum_{\vec{q}}C_{V,\vec{q}\lambda}^{op}} \tag{2}$$

where $C_{V,\vec{q}\lambda}^{ac,op} = k_B\left(\frac{\hbar\omega_{\vec{q}\lambda}}{k_BT}\right)^2 \exp\left(\frac{\hbar\omega_{\vec{q}\lambda}}{k_BT}\right)\left[\exp\left(\frac{\hbar\omega_{\vec{q}\lambda}}{k_BT}\right)-1\right]^{-2}$ is the isochoric specific heat for the normal mode $i = \vec{q}\lambda$ (acoustic and optical, respectively) and the denominator expresses the total isochoric heat, $C_V = C_V^{ac} + C_V^{op}$. The numerator of the expression (2) cannot be evaluated without some approximations. For evaluation, we shall consider the acoustic and optical vibrational frequencies expressed by some Debye's $\Theta_D(T)$ and Einstein's $\Theta_E(T)$ temperatures, these dependences being obtained by fitting the theoretical curves with the experimental data for $C_V^{ac}(T)$ and $C_V^{op}(T)$ [9].

Therefore, considering for acoustic vibrations $\hbar\omega_{\max} = k_B\Theta_D$ and for optical vibrations $\hbar\omega_E = k_B\Theta_E$, where k_B and $h = 2\pi\hbar$ are Boltzmann and Planck constants, respectively, one gets

$$\gamma^{ac}\left(\frac{\Theta_D}{T}\right) = -\frac{d\ln\Theta_D(T)}{d\ln V}; \qquad \gamma^{op}\left(\frac{\Theta_E}{T}\right) = -\frac{d\ln\Theta_E(T)}{d\ln V} \tag{3}$$

This means that acoustic and optical Grüneisen's parameters are considered as depending themselves of the temperature T through Debye's and Einstein's temperature dependences, and, at the same time, allows the evaluation of numerator from the expression (2). Thus, for the considered dispersion laws and after some corelations [10] one gets the total Grüneisen's parameter

$$\gamma\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right) = \frac{\gamma^{ac}\left(\frac{\Theta_D}{T}\right)F_D\left(\frac{\Theta_D}{T}\right) + (s-1)\gamma^{op}\left(\frac{\Theta_E}{T}\right)F_E\left(\frac{\Theta_E}{T}\right)}{F_D\left(\frac{\Theta_D}{T}\right) + (s-1)F_E\left(\frac{\Theta_E}{T}\right)} \tag{4}$$

where

$$F_D\left(\frac{\Theta_D}{T}\right) = 3\left(\frac{T}{\Theta_D}\right)^3\int_0^{\frac{\Theta_D}{T}}\frac{x^4\exp(x)dx}{[\exp(x)-1]^2}; \quad F_E\left(\frac{\Theta_E}{T}\right) = \left(\frac{\Theta_E}{T}\right)^2\frac{\exp\left(\frac{\Theta_E}{T}\right)}{\left[\exp\left(\frac{\Theta_E}{T}\right)-1\right]^2} \tag{5}$$

are Debye's and Einstein's functions, respectively. If we introduce the ratio

$$\beta\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right) = \frac{C_V^{op}\left(\frac{\Theta_E}{T}\right)}{C_V^{ac}\left(\frac{\Theta_D}{T}\right)} = (s-1)\frac{F_E\left(\frac{\Theta_E}{T}\right)}{F_D\left(\frac{\Theta_D}{T}\right)} \tag{6}$$

total Grüneisen's parameter for a solid with polyatomic basis becomes

$$\gamma\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right) = \frac{\gamma^{ac}\left(\frac{\Theta_D}{T}\right) + \beta\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right)\gamma^{op}\left(\frac{\Theta_E}{T}\right)}{1+\beta\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right)} \tag{7}$$

Concerning to the values of s, one may see that $\gamma\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right) = \gamma^{ac}\left(\frac{\Theta_D}{T}\right)$ for a crystal with simple lattice ($s=1$) and $\gamma\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right) \cong \gamma^{op}\left(\frac{\Theta_E}{T}\right)$ for that with polyatomic basis ($s>>1$), the inequalities $\gamma^{ac}\left(\frac{\Theta_D}{T}\right) \le \gamma\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right) \le \gamma^{op}\left(\frac{\Theta_E}{T}\right)$ being satisfied too. Regarding the temperature values, for low temperatures, because $F_E\left(\frac{\Theta_E}{T}\right) << F_D\left(\frac{\Theta_D}{T}\right)$, we have $\gamma\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right) = \gamma^{ac}\left(\frac{\Theta_D}{T}\right)$, i.e., total Grüneisen's parameter is determined practically by the acoustic phonons. In the intermediate temperatures range, because $F_E\left(\frac{\Theta_E}{T}\right) < F_D\left(\frac{\Theta_D}{T}\right)$, for $s>>1$, one gets

$\gamma\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right)\cong\beta\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right)\left[1+\beta\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right)\right]^{-1}\gamma^{op}\left(\frac{\Theta_E}{T}\right)$, i.e., only a small contribution of acoustic phonons may be considered. At last, for high temperatures, because $F_E\left(\frac{\Theta_E}{T}\right)\to F_D\left(\frac{\Theta_D}{T}\right)$ and $\beta\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right)\to 1$, for $s>>1$, one gets $\gamma\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right)\cong\gamma^{op}\left(\frac{\Theta_E}{T}\right)$, i.e., total Grüneisen's parameter is determined practically by optical phonons.

Taking into account total Grüneisen's parameter in a solid with polyatomic basis one may obtain easily the well-known thermodynamical expression for the isobaric linear expansion coefficient $\alpha_P=\frac{1}{3V}\left(\frac{dV}{dT}\right)_P$, including both the contributions of acoustic and optical vibrations, respectively. Thus,

$$\alpha_P\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right)=\frac{3C_V\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right)\gamma\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right)}{3VB_T}=\frac{k_BN\left[F_D\left(\frac{\Theta_D}{T}\right)+(s-1)F_E\left(\frac{\Theta_E}{T}\right)\right]}{VB_T} \tag{8}$$

where $C_V\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right)=C_V^{ac}\left(\frac{\Theta_D}{T}\right)+C_V^{op}\left(\frac{\Theta_E}{T}\right)$ and $B_T=-V\left(\frac{dP}{dV}\right)_T$ is the isothermal bulk modulus and N is the total number of atoms in a crystal of volume V. Because the isothermal bulk modulus for many solids presents only a very small temperature dependence, increasing gradually when the temperature decreases, in the first approximation it may be considered constant. Also, taking into account the temperature dependence of the functions $F_D\left(\frac{\Theta_D}{T}\right)$ and $F_E\left(\frac{\Theta_E}{T}\right)$ one may obtain the well-known results $\alpha_P\sim\left(\frac{T}{\Theta_D}\right)^3$ for low temperatures, and it changes very little in the high temperatures range so that in a rough approximation $\alpha_P\approx const.$ [10]. At last, we emphasize that the above results include implicitly the vibrational anharmonicity effects through the temperature dependence of Grüneisen's parameters and of the volume thermal expansion coefficient.

3. Results and discussion

In order to analyse the temperature dependence of Grüneisen's parameters in the case of a solid with polyatomic basis ($s>>1$) we shall refer to the undoped bismuth silicon oxyde ($Bi_{12}SiO_{20}$) crystal, with $s=66$ atoms in an elementary cell, for high temperatures between $300\,K$ and $900\,K$ where the study of the specific heats [9] indicates on the predominant role played by the optical vibrations. In this case, the relation (8) gives the optical Grüneisen's parameter as:

$$\gamma^{op}\left(\frac{\Theta_E}{T}\right)=\frac{\alpha_P\left(\frac{\Theta_E}{T}\right)VB_T}{k_BN(s-1)F_E\left(\frac{\Theta_E}{T}\right)}=\frac{3\alpha_P\left(\frac{\Theta_E}{T}\right)VB_T}{C_V^{op}\left(\frac{\Theta_E}{T}\right)} \tag{9}$$

Replacing the experimental values $C_{V,ex}^{op}\left(\frac{\Theta_E}{T}\right)$ from [9] and considering a weak temperature dependence of the isobaric thermal expansion coefficient $\alpha_P\left(\frac{\Theta_E}{T}\right)\approx\alpha_P(300\,K)=1.5\times10^{-6}\,K^{-1}$, one obtains the experimental dependence of optical

Grüneisen's parameter $\gamma_{ex}^{op}\left(\frac{\Theta_E}{T}\right)$, plotted in Fig. 1 with circles. On the other hand, replacing the experimental values of the total isochoric specific heat $C_{V,ex}(\frac{\Theta_D}{T},\frac{\Theta_E}{T}) = C_{V,ex}^{ac}(\frac{\Theta_D}{T}) + C_{V,ex}^{op}(\frac{\Theta_E}{T})$ from [9] and considering that $\alpha_P(\frac{\Theta_D}{T},\frac{\Theta_E}{T}) \approx \alpha_P(\frac{\Theta_E}{T})$ we obtain the experimental dependence of total Grüneisen's parameter $\gamma_{ex}\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right)$, plotted in Fig. 1 by filled dots. At last, we evaluate the theoretical temperature dependence of total Grüneisen's parameter, $\gamma_{calc}\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right)$ using the theoretical values $C_{V,ccalc}(\frac{\Theta_D}{T},\frac{\Theta_E}{T}) = C_{V,calc}^{ac}(\frac{\Theta_D}{T}) + C_{V,calc}^{op}(\frac{\Theta_E}{T})$ and taking the values $\Theta_D(300\,K) = 293\,K$ and $\Theta_E(300\,K) = 774\,K$, [9], respectively. This dependence is plotted in Fig. 1 by a continuous curve. A comparison of these curves points out that the experimental values of total Grüneisen's parameter $\gamma_{ex}\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right)$ are in very good agreement with those calculated $\gamma_{calc}\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right)$ in the whole considered temperature range. Also, these values are in satisfactory agreement with those for $\gamma_{ex}^{op}\left(\frac{\Theta_E}{T}\right)$ suggesting the predominant role played by the optical vibrations for undoped $Bi_{12}SiO_{20}$ crystal in the considered temperature range. The above results may be compared with those obtained in Debye approximation assuming that all $3Ns$ vibrations are acoustic. In this case using an expression similar to (9) with $C_{V,ex}(\frac{\Theta_D}{T},\frac{\Theta_E}{T}) \to C_{V,ex}^{ac}(\frac{\Theta_D}{T})$ from [9] we obtain the experimental values for $\gamma_{ex}^{ac}\left(\frac{\Theta_D}{T}\right)$ which are plotted in Fig. 1 by filled triangles. One observes the departure between the values of $\gamma_{ex}^{ac}\left(\frac{\Theta_D}{T}\right)$ and those given by $\gamma_{ex}\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right) \cong \gamma_{ex}^{op}\left(\frac{\Theta_E}{T}\right)$ this difference being significant for lower temperatures. One may remark also that all these Grüneisen's parameters decrease when the temperature increases and this behaviour may be connected with the above mentioned "implicit" and "explicit" temperature variations of the vibrational frequency. Thus, the temperature dependence of Grüneisen's parameters in a normal solid (without phase transition or magnetovolume effect) must be associated with the temperature dependence of the i-th phonon-mode frequency, which may be taken as $\omega_i(T) = \omega_i(0) + a_1 T + a_2 T^2$ where $\omega_i(0)$ is the phonon frequency at $T = 0\,K$ with a_1 and a_2 being some constants [11-13]. For high temperatures range, as that considered in this work, a linear temperature dependence of $\omega_i(T)$ could be considered as a good approximation, so that $a_2 = 0$. Then,

$$\omega_i(T) = \omega_i(0) + \left(\frac{d\omega_i}{dT}\right)_P dT = \omega_i(0) + a_1 T \tag{10}$$

where $a_1 = \left(\frac{d\omega_i}{dT}\right)_P > 0$ because $\omega(T)$ is an increasing function both for acoustic and optical vibrations and the initial temperature has been considered $T_0 = 0\,K$. The anharmonic shifts of the frequencies are positive and increase with temperature. The hypothesis on the frequency shift gives results in agreement with the diagrams of $\Theta_D(T)$ and $\Theta_E(T)$ plotted in [9] and reproduced here in the inset of Fig. 1. On the other hand, the "implicit" volume dependence of the phonon frequencies

$\omega_i = \omega_i(V)$ which generally is a decreasing function may be considered also in the linear approximation given by

$$\omega_i(V) = \omega_i(V_0) + \left(\frac{d\omega_i}{dV}\right)_P dV = \omega_i(V_0) + b_1(V - V_0) \tag{11}$$

where V_0 is the crystal volume at $T = 0\,K$ and $b_1 = \left(\frac{d\omega_i}{dV}\right)_P < 0$, in agreement with the physical considerations and with the condition that Grüneisen's parameter is positive, $\gamma_i > 0$. In the frame of above considerations the temperature dependence $\gamma_i = \gamma_i(T)$ of Grüneisen's parameter in the linear approximation may be written

$$\gamma_i(T) = \gamma_i(0) + \left(\frac{d\gamma_i}{dT}\right)_P dT = \gamma_i(0) + \left(\frac{\partial\gamma_i}{\partial T}\right)_P T \tag{12}$$

where $\gamma_i(0)$ is Grüneisen's parameter at the initial temperature $T_0 = 0\,K$. Taking into account the dependence of the frequency versus the temperature $\omega_i(T)$ through both the "implicit" contribution due to thermal expansion $\left(\frac{d\omega_i}{dV}\right)_T\left(\frac{dV}{dT}\right)_P$ and the "explicit" contribution due to vibrational anharmonicity at constant volume $\left(\frac{d\omega_i}{dT}\right)_V$ [7], the relation (12) becomes

$$\gamma_i(T) = \gamma_i(0) + \left(\frac{d\gamma_i}{d\omega_i}\right)_P\left[\left(\frac{d\omega_i}{dV}\right)_T\left(\frac{dV}{dT}\right)_P + \left(\frac{d\omega_i}{dT}\right)_V\right]T \tag{13}$$

Considering also the isobaric thermal expansion coefficient $\alpha_P(T) = \frac{1}{3V}\left(\frac{dV}{dT}\right)_P$, one obtains the expression

$$\gamma_i(T) = \gamma_i(0) - c_1 T \tag{14}$$

where

$$c_1 = -\frac{V}{\omega_i^2} b_1\left[3\alpha_P(T)Vb_1 + a_1\right] \tag{15}$$

with $a_1 > 0,\ b_1 < 0,\ \alpha_P(T) > 0$. Therefore, one obtains $c_1 > 0$ when the inequality $a_1 > 3\alpha_P(T)V|b_1|$ is fulfilled, i.e., for high temperatures range the term describing the vibrational anharmonic contribution at constant volume predominates over that describing directly the thermal expansion contribution. Thus, in the case when the solid expansion with temperature, the Grüneisen's parameters decrease with the temperature as we have obtained for undoped $Bi_{12}SiO_{20}$ crystal, both for acoustic $\gamma^{ac}(T)$ and optical $\gamma^{op}(T)$ in the considered high temperature range. The fact that vibrational anharmonicity contribution, considered here in a semiempirical way through the temperature dependence of Debye's $\Theta_D(T)$ and Einstein's $\Theta_E(T)$ temperatures, may be used also to justify the more pronounced decreasing with the temperature for $\gamma^{op}(T)$ than for $\gamma^{ac}(T)$. Otherwise, if the reverse inequality $a_1 < 3\alpha_P(T)V|b_1|$ is fulfilled, i.e., the effect of volume expansion prevails over that of vibrational anharmonicity, which is expected for a low temperatures range, one gets

$c_1 < 0$ and Grüneisen's parameters increase with the temperature. Such behaviour has been usually accepted for acoustic Grüneisen's parameter $\gamma^{ac}(T)$ [1].

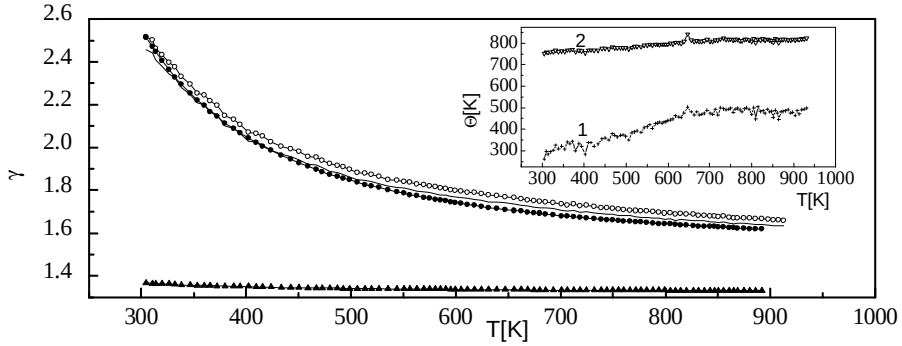

Fig. 1. The temperature dependence of Grüneisen's parameters for undoped $Bi_{12}SiO_{20}$ crystal: (••••) $\gamma_{ex}\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right)$; (——) $\gamma_{calc}\left(\frac{\Theta_D}{T},\frac{\Theta_E}{T}\right)$; (○○○○) $\gamma_{ex}^{op}\left(\frac{\Theta_E}{T}\right)$; (▲▲▲▲) $\gamma_{ex}^{ac}\left(\frac{\Theta_D}{T}\right)$. In the inset: Debye's $\Theta_D(T)$ (curve 1) and Einstein's $\Theta_E(T)$ (curve 2) from [9].

The temperature dependence of Grüneisen's parameters presents a different behaviour in the case when the crystal is characterized by contraction with temperature. Thus, the relation (14) maintains its form but with $a_1 > 0$, $b_1 > 0$, $\alpha_P(T) < 0$. As a result, the vibrational anharmonicity effect prevails over the thermal contraction effect when the inequality $a_1 > 3|\alpha_P(T)|Vb_1$ is fulfilled and leads to $c_1 < 0$. Therefore, Grüneisen's parameters increase with the temperature and such behaviour has been observed for some alkali halides [11]. Obviously, if the reverse inequality $a_1 < 3|\alpha_P(T)|Vb_1$ is fulfilled in the case of a low temperatures range, i.e., the effect of volume constriction prevails over that of vibrational anharmonicity, one obtains $c_1 > 0$. As a result, it is possible a situation when Grüneisen's parameters decrease with the temperature. These considerations allow to explain qualitatively the temperature dependence of Grüneisen's parameters but are limited by the linear approximation used in the series developments. Indeed, if we maintain the linear approximation for the temperature dependence of the crystal volume given by the coefficient $\alpha_P(T)$ and we consider the competition between volume and anharmonicity lattice effects, the case given by the equality $\left(\frac{d\omega_i}{dV}\right)_T\left(\frac{dV}{dT}\right)_P\left(\frac{dT}{d\omega_i}\right)_V = -1$ leads to the simple conclusion about the compensation of those effects, i.e., Grüneisen's parameters does not depend of the temperature: $\gamma_i(T) = const$. However, at the same time, the considered equality leads to the conclusion that the vibrational frequency $\omega_i(V,T) = const.$ which is difficult to be accepted. Therefore, a nonlinear dependence in the series development of $\omega_i = \omega_i(V)$, $\omega_i = \omega_i(T)$ and $\gamma_{i=}\gamma_i(T)$ is desirable to be considered even if the anharmonicity effets are treated in a semiempirical way through the temperature dependence of Debye's $\Theta_D(T)$ and Einstein's $\Theta_E(T)$ temperatures.

Another fact which must be remarked is that the predominant role played by optical vibrations in the high temperature range cannot be considered as a general conclusion for any crystal with polyatomic basis. Indeed, the Debye-Einstein approximation is valid only in the case when the vibrational spectrum of a solid with polyatomic basis cannot be described solely by acoustic vibrations and, respectively, by a Debye's temperature $\Theta_D(T)$. Thus, there are some solids with polyatomic basis as MgO, $MgSiO_3$, Al_2O_3 and other [1] for which the consideration only of the acoustic frequency corresponding to Debye's temperature $\Theta_D(T)$ leads to results which agree satisfactorily with the experimental data.

4. Conclusion

In a solid with polyatomic basis, in the high temperature range, the total Grüneisen's parameter is given practically by optical Grüneisen's parameter $\gamma^{op}(T)$. Both $\gamma^{op}(T)$ and $\gamma^{ac}(T)$ parameters decrease when the temperature increases. This behaviour results from the competition between the volume and lattice anharmonicity effects of the temperature on the phonon frequencies shifts. The anharmonicity effects prevails over the volume contribution and this effect is more pronounced for optical than acoustic vibrations.

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