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Ultrasonic attenuation in molecular crystals

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It is now well established from an experimental point of view that, concerning the ultrasonic attenuation, molecular crystals exhibit a specific behavior among dielectric crystals. This fact suggests the presence of a relaxation process. Liebermann, who has introduced this field, has proposed a way to analyze this problem and in particular has given an expression for the ultrasonic absorption coefficient in terms of a relaxation time and some thermodynamic quantities. In contrast to Liebermann's approach, a solid-state viewpoint is presented here, and it is shown that this ultrasonic relaxation can be taken into account in the framework of Akhieser's theory. A general expression of the ultrasonic absorption coefficient is calculated in terms of the phonon collision operator using the Boltzmann-equation approach of Woodruff and Ehrenreich. The collision-time approximation widely used in dielectric crystals fails in molecular crystals for which the presence of slow relaxation times in the collision operator prevents the thermalization of the whole set of phonons and gives rise to an ultrasonic relaxation. Thus a more suitable approximation is suggested here, which leads to a new expression of the ultrasonic attenuation valid in molecular crystals. Different forms of this expression are discussed, and comparison with Liebermann's expression used in most of the previous papers shows that the present treatment takes better account of the anisotropy of the solid state. The fit of experimental results obtained for some ionic-molecular crystals also shows that the expression derived here gives better agreement than does Liebermann's. Finally, it is shown that in the framework of the present treatment and under rather general conditions, the anisotropy affects primarily the magnitude of the ultrasonic absorption due to the molecular relaxation, but it does not affect its frequency dependence.

I. INTRODUCTION

Although molecular crystals belong to the family of dielectric crystals, they exhibit special behavior with regard to ultrasonic absorption. The first mention of this was a theory by Liebermann[1] in 1959, who proposed the extension to the solid state of a well-known phenomenon which arises in molecular gases and liquids: A relaxation may occur in these compounds due to a slow transfer of energy between internal and external degrees of freedom of molecules which belong to a population perturbed by an ultrasonic wave. This extension raises two distinct problems.

The first is the derivation of a relation between the ultrasonic absorption coefficient α and the time τ characterizing the relaxation. Concerning this problem, Liebermann does not adopt a solid-state viewpoint and is content with using a relation derived by Richards[2] considering specific properties of the equations of state of gases and liquids:

$$\alpha=\frac{1}{2s}\frac{C_P-C_V}{C_P}\frac{C_I}{C_P-C_I}\frac{\Omega^2\tau}{1+\Omega^2\tau^2} . \qquad (1)$$

Here Ω and s are, respectively, the angular frequency and the velocity of the ultrasonic wave, C_P and C_V are the specific heats per unit volume at constant pressure and constant volume, respectively, and C_I is the specific heat associated with the internal degrees of freedom. As the solid state possesses properties rather different from those of the gas or liquid phases concerning the propagation of ultrasonic waves the use of the relation (1) in molecular crystals seems questionable.

The second problem is the derivation of an expression of τ in terms of characteristic parameters of the crystal. For this purpose Liebermann proposes a model built on many approximations, so that it may lead to large discrepancies with experimental determinations of τ. However, we will not speak about this problem in our paper.

After Liebermann's paper, some works [mostly experimental (Refs. 3 – 18)] have appeared on this subject from which we can deduce the following points.

α in molecular compounds which have been investigated is abnormally large for dielectric crystals;

The dependence of α on frequency and temperature is unusual and suggests the presence of a relaxation process;

At room temperature the observed relaxation times are roughly about one nanosecond.

From a theoretical point of view Danielmeyer[9] and later Victor and Beyer[13] try to take into account the actual nature of the solid phase, but they use a very phenomenological approach to derive the relation between α and τ. Moreover, in all the papers on this subject the anomalous behavior of ultrasonic attenuation in molecular crystals has been considered as resulting from a new phenomenon compared with the different mechanisms of ultrasonic absorption which have been previously identified in dielectric crystals.

In this paper, after a short comment about the classical theories of ultrasonic attenuation in dielectric crystals, we briefly sketch the different steps of the derivation of Akhieser's theory[19] and obtain a general expression of α in the hydrodynamical regime of propagation of sound. We show that the collision-time approximation, which is generally used with dielectric crystals, fails with molecular crystals. We devise a more sophisticated approximation appropriate to these crystals. Through this method we get a new expression for α in molecular crystals and compare it with that of Liebermann. Finally, in the last section of this paper we try to draw some conclusions about the influence of anisotropy on this phenomenon of relaxation.

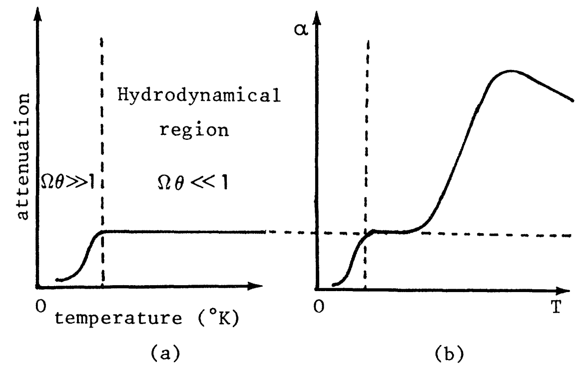
II. A FEW WORDS ABOUT CLASSICAL THEORIES

There are schematically two classical descriptions of the ultrasonic absorption in dielectric crystals. These models roughly correspond to two frequency ranges separated by $1/\Theta$, where Θ is the mean lifetime of thermal phonons (at room temperature Θ is typically a few picoseconds).

In the high-frequency range ($\Omega\Theta >> 1$) the suitable approach was first suggested by Landau and Rumer,[20] who consider the ultrasonic wave as an excess of phonons in the mode $(\vec{K},\vec{e})$ ($\vec{K}$ is the unit wave vector of sound, $\vec{e}$ is the polarization). In this theory ultrasonic attenuation is seen as resulting from a direct interaction between thermal phonons and phonons in the mode $(\vec{K},\vec{e})$.

In the low-frequency range ($\Omega\Theta << 1$), it is more convenient to follow the method introduced by Akhieser,[19] who considers the ultrasonic wave as an external field which modulates in space and time the population of thermal phonons. In this approach the relaxation of phonons in finite times (generally about Θ) towards new equilibrium distributions gives rise to ultrasonic attenuation.

These two approaches give a good basis for the analysis of sound absorption in dielectric crystals over the whole range of temperature and frequency. Nevertheless, we have already noticed that some of the major predictions obtained from these two approaches are violated in molecular crystals. An example of this violation is represented in Fig. 1, where the temperature dependence of α is given in what we can call (following Victor *et al.*[12]) a "hard" dielectric crystal and in a molecular crystal. As the respective orders of magnitude of Θ and τ are very different, this anomaly is entirely located in the hydrodynamical region, so that it can be explained only by theories adapted to the low-frequency range. Consequently, we will now follow a method parallel to that pioneered by Akhieser and improved upon by Woodruff and Ehrenreich.[21] In this way we will show that the specific properties of molecular crystals can be taken into account by using a single formalism valid for any dielectric crystal.



(a) (b)

FIG. 1. Trends of the temperature dependence of the ultrasonic attenuation in (a) a "hard" dielectric crystal and in (b) a molecular crystal.

Although the first steps of Akhieser's approach are now well known, we will recall them in the next section to introduce a vector notation that enables us to get a general expression of α in terms of the phonon collision operator without any approximation of this operator.

III. GENERAL EXPRESSION OF THE ULTRASONIC ABSORPTION COEFFICIENT

We must localize phonons inside a volume V, which characterizes the local scale of our problem. Whatever the state of deformation of the lattice, we decide that a phonon with wave vector $\vec{k}$, polarization σ, and frequency $\omega_\lambda(\vec{x},t)$ corresponds to a set of constant integers in the reference frame of the reciprocal lattice, and we index it by the Greek letter λ.

Without any deformation of the lattice the equilibrium distribution n_λ of phonons λ is uniform, and we have

$$n_\lambda=\frac{1}{e^{\beta\hbar\omega_\lambda}-1}\quad\text{with}\quad\beta=\frac{1}{k_BT}\ . \tag{2}$$

The local deformation $\eta(\vec{x},t)$ due to the propagation of an ultrasonic wave defined by its amplitude $\vec{u}(\vec{x},t)$ induces a local shift of the frequency ω_λ of phonons, so that

$$\omega_\lambda(\vec{x},t)=\omega_\lambda[1-\gamma_{\lambda,ij}\eta_{ij}(\vec{x},t)]\ , \tag{3}$$

where $\gamma_{\lambda,ij}$ is a component (i,j) of the Grüneisen tensor linked to a phonon λ. With such a deformation the equilibrium distribution of phonons would be

$$\bar{n}_\lambda(\vec{x},t)=\frac{1}{e^{\beta(\vec{x},t)\hbar\omega_\lambda(\vec{x},t)}-1} \tag{4}$$

with

$$\beta(\vec{x},t)=\frac{1}{k_BT(\vec{x},t)}=\frac{1}{k_B[T+\Delta T(\vec{x},t)]}\ . \tag{5}$$

However, due to finite relaxation times, the distribution $\bar{n}_\lambda(\vec{x},t)$ cannot be reached and the actual distribution is $N_\lambda(\vec{x},t)$. If we set

$$\begin{aligned}N_\lambda(\vec{x},t)&=\bar{n}_\lambda(\vec{x},t)+\overline{\Delta N}_\lambda(\vec{x},t)\\&=n_\lambda+\Delta N_\lambda(\vec{x},t)\ ,\end{aligned} \tag{6}$$

then to the first order in strain we find

$$\overline{\Delta N}_\lambda-\Delta N_\lambda=-\left[\gamma_{\lambda,ij}\eta_{ij}(\vec{x},t)+\frac{\Delta T(\vec{x},t)}{T}\right]\times\frac{\hbar\omega_\lambda}{k_BT}n_\lambda(n_\lambda+1)\ . \tag{7}$$

For any quantity $f(\vec{x},t)$ we look for solutions in the form of plane waves $(\vec{K},\Omega')$ and we set

$$f(\vec{x},t)=fe^{i\Omega'[t-(\vec{K}\cdot\vec{x})/s]}\ , \tag{8}$$

where $\mathrm{Re}(\Omega')=\Omega$, and $\mathrm{Im}(\Omega')$ gives rise to the attenuation α. Thus we have

$$u_i(\vec{x},t)=ue_ie^{i\Omega'[t-(\vec{K}\cdot\vec{x})/s]}\ . \tag{9}$$

With these notations it can be shown[22] that the attenuation α is related to ΔN_λ through the equation

$$\alpha=-\frac{\hbar}{2\rho Vs^2}\sum_\lambda\gamma_\lambda\omega_\lambda\mathrm{Re}\left[\frac{\Delta N_\lambda}{u}\right]\ , \tag{10}$$

where ρ is the density and where we have set

$$\gamma_\lambda=\gamma_{\lambda,ij}e_iK_j\ . \tag{11}$$

To describe the evolution of phonons and determine ΔN_λ, we use a Boltzmann equation

$$\frac{\partial N_\lambda}{\partial t}+\frac{1}{\hbar}\left[\frac{\partial N_\lambda}{\partial x_i}\frac{\partial H_\lambda}{\partial k_i}-\frac{\partial N_\lambda}{\partial k_i}\frac{\partial H_\lambda}{\partial x_i}\right]=\left[\frac{\partial N_\lambda}{\partial t}\right]_{\text{coll}}\ , \tag{12}$$

where the left- and right-hand sides describe, respectively, the dynamics of a phonon λ and its interactions with the other phonons. It can be shown[23] that the Hamiltonian of a single phonon λ is

$$H_\lambda(\vec{x},t)=\hbar\omega_\lambda(\vec{x},t)\ . \tag{13}$$

To first order in strain (which is typically about $10^{-7}-10^{-5}$ in standard experiments) Eq. (12) becomes

$$\frac{\partial\Delta N_\lambda}{\partial t}+v_{\lambda,i}\frac{\partial\Delta N_\lambda}{\partial x_i}-\beta\hbar\omega_\lambda n_\lambda(n_\lambda+1)v_{\lambda,i}\gamma_{\lambda,kj}\frac{\partial\eta_{kj}}{\partial x_i}=M_{\lambda\lambda'}\overline{\Delta N}_{\lambda'}\ , \tag{14}$$

where $M_{\lambda\lambda'}$ is a component of the phonon collision operator M which contains all the information about the relaxation of phonons and $\vec{v}_\lambda$ is the group velocity of phonons λ.

It seems to us that the Boltzmann equation is rigorous only in its linearized form (14) because of complications when we go beyond the first order in strain. For example, we have to choose between Eulerian and Lagrangian coordinates, not only for the direct lattice but also for the reciprocal lattice. A consequence of these difficulties has been the erroneous introduction of the rotation of the medium in Eq. (3) by Akhieser[19] and then by Woodruff and Ehrenreich,[21] which would lead to a loss of symmetries of the macroscopic viscosity tensor. Thus, the problem of the evolution equation for higher orders probably cannot be solved by a straightforward Taylor expansion of Eq. (12).

To go further without any approximation we follow Maris[24] by introducing a vector notation and using general properties of collision operator. We define a vector space F of $\mathcal{N}$ dimensions (where $\mathcal{N}$ is the number of modes) so that any quantity $L_{\lambda_1 \cdots \lambda_p}$ can be considered such as a component of a pth rank tensor L on F.

It can be seen[25] that the operator $\widetilde{M}$ defined by

$$\widetilde{M}_{\lambda\lambda'} = \left[\frac{n_{\lambda'}(n_{\lambda'}+1)}{n_\lambda(n_\lambda+1)} \right]^{1/2} M_{\lambda\lambda'} \tag{15}$$

is symmetric. Moreover, this operator obeys a conservation law for the total energy of the phonon system valid to the first order in strain (this property can be directly viewed as a consequence of the fact that the deformation energy is quadratic in strain). Thus we have

$$\sum_\lambda \hbar\omega_\lambda \left[\frac{\partial N_\lambda}{\partial t} \right]_{\text{coll}} = \sum_{\lambda\lambda'} \hbar\omega_\lambda M_{\lambda\lambda'} \overline{\Delta N}_{\lambda'} = 0 \,. \tag{16}$$

Then

$$\sum_{\lambda\lambda'} \hbar\omega_\lambda [n_\lambda(n_\lambda+1)]^{1/2} \times \widetilde{M}_{\lambda\lambda'} [n_{\lambda'}(n_{\lambda'}+1)]^{-1/2} \overline{\Delta N}_{\lambda'} = 0 \,. \tag{17}$$

Using the symmetry of $\widetilde{M}$ we deduce from (17) that the normalized vector X_1, whose components are $\hbar\omega_\lambda[n_\lambda(n_\lambda+1)\beta/TC]^{1/2}$, is a zero eigenvalue eigenvector of $\widetilde{M}$. We have set

$$C = \sum_{\lambda \in F} \frac{\beta(\hbar\omega_\lambda)^2}{T} n_\lambda(n_\lambda+1) \,. \tag{18}$$

In the quasiharmonic approximation C_V, the specific heat at constant volume, is equal to C/V. With the help of these different properties we obtain a compact form for the Boltzmann equation,

$$\widetilde{M} \left[\Delta\widetilde{N} + i\frac{\Omega u}{s}\widetilde{\gamma} \right] = i\Omega(I-\xi)(\Delta\widetilde{N}) + \frac{\Omega^2 u}{s}\xi(\widetilde{\gamma}) \,, \tag{19}$$

where

$$\Delta\widetilde{N}_\lambda = [n_\lambda(n_\lambda+1)]^{-1/2} \Delta N_\lambda \,, \tag{20}$$

and

$$\widetilde{\gamma}_\lambda = \beta\hbar\omega_\lambda [n_\lambda(n_\lambda+1)]^{1/2} \gamma_\lambda \,. \tag{21}$$

I is the unit operator, and the operator ξ is given by

$$\xi_{\lambda\lambda'} = \frac{\vec{v}_\lambda \cdot \vec{K}}{s} \delta_{\lambda\lambda'} \,. \tag{22}$$

Thus we get the expression of $\Delta\widetilde{N}$ in vector notation

$$\Delta\widetilde{N} = -\frac{i\Omega u}{s}(I + i\widehat{M})(\widetilde{\gamma}) \tag{23}$$

with

$$\widehat{M} = \Omega[\widetilde{M} - i\Omega(I-\xi)]^{-1} \,. \tag{24}$$

(For any operator L, L^{-1} is the inverse operator.) Finally, we deduce a general expression for α,

$$\alpha = -\frac{\Omega}{2\rho V s^3} \frac{1}{\beta} \text{Re}[(\widetilde{\gamma} \cdot \widehat{M}(\widetilde{\gamma}))_F] \,, \tag{25}$$

where $(\ )_F$ means the scalar product on F.

IV. THE COLLISION-TIME APPROXIMATION

Now we introduce the following simplification to get an easier derivation: We will no longer take into account the term $i\Omega\xi$. In the Appendix we discuss a derivation of the results obtained in this paper without this simplification but only in the hydrodynamical region ($\Omega\Theta << 1$). We show that accounting for the group velocities of phonons leads to the introduction in the expression of α of an additive term which may be identified with the classical thermoelastic loss. The same result has been previously derived under the collision-time approximation.[22]

With this simplification $\widehat{M}$ and $\widetilde{M}$ have the same eigensubspaces. Let $-1/\tau_i$ ($i > 1$) be the nonzero eigenvalues of $\widetilde{M}$ (since $\widetilde{M}$ is a symmetric operator, these eigenvalues are real) and X_i the corresponding normalized eigenvectors. The eigenvalues of $\widehat{M}$

are $-\Omega\tau_i/(1+i\Omega\tau_i)$, so that α is given by

$$\alpha=\frac{1}{2\rho V s^3}\frac{1}{\beta}\sum_{i>1}\left[\frac{\Omega^2\tau_i}{1+\Omega^2\tau_i^2}(\tilde{\gamma}\cdot X_i)_F^2\right] . \tag{26}$$

(We must keep in mind that $\Omega\Theta<<1$, where Θ is of the order of magnitude of the faster relaxation times τ_i.)

In the collision-time approximation we usually assume that $\tilde{M}$ has the simple form

$$\tilde{M}_{\lambda\lambda'}=-\frac{1}{\Theta}\delta_{\lambda\lambda'} . \tag{27}$$

This is slightly incorrect because we know that 0 is an eigenvalue of $\tilde{M}$; moreover, this formulation entails the determination of $\Delta T(\vec{x},t)$. In fact, in this approximation we have two eigenvalues: 0 and $1/\Theta$. The eigensubspace G associated with $-1/\Theta$ has a degeneracy equal to $\mathcal{N}-1$. Thus α is given by

$$\alpha=\frac{1}{2\rho V s^3}\frac{1}{\beta}\{\Omega^2\Theta[\tilde{\gamma}-(\tilde{\gamma}\cdot X_1)_F X_1]^2\} . \tag{28}$$

[For any vector g of F, g^2 means $(g\cdot g)_F$.]

We make the two following definitions:

$$\langle\gamma\rangle=\frac{\beta}{TC}\sum_{\lambda\in F}(\hbar\omega_\lambda)^2 n_\lambda(n_\lambda+1)\gamma_\lambda \tag{29}$$

and

$$\langle\gamma^{(2)}\rangle=\frac{\beta}{TC}\sum_{\lambda\in F}(\hbar\omega_\lambda)^2 n_\lambda(n_\lambda+1)\gamma_\lambda^2 , \tag{30}$$

which lead to the well-known expression of α:

$$\alpha=\frac{C_V T}{2\rho s^3}(\langle\gamma^{(2)}\rangle-\langle\gamma\rangle^2)\Omega^2\Theta . \tag{31}$$

V. SPECIFICITY OF MOLECULAR CRYSTALS

The collision-time approximation, which is widely used in dielectric crystals, fails in the case of molecular crystals in which there could coexist two very different orders of magnitude among relaxation times. Thus, to support the proposition of Liebermann with a solid-state point of view we suggest the following description of the behavior of phonons in molecular crystals. In these crystals there are two groups of modes, external and internal modes, corresponding, respectively, to the external and internal degrees of freedom of molecules (and defining, respectively, the two subspaces E and I in F). Now we assume that inside each group of modes we have strong interactions defined by fast relaxation times ($\sim\Theta$) but that these two groups are only weakly linked with slow relaxation times ($\sim\tau$). By this way an ultrasonic experiment can be described such as in Fig. 2.

This model is consistent with the addition of a third eigenvalue $-1/\tau$ to the collision operator. Now we have to determine in a unique way the subspace associated with $-1/\tau$. The following conditions lead to the determination of a single eigenvector X_3.

(i) We consider that within the scale of Θ times we have conservation of the total energies U_E and U_I of, respectively, external and internal phonon systems (in other words, we work under the assumption $\Theta/\tau<<1$). Thus (17) is valid for the restrictions of $\tilde{M}$ in the two subspaces E and I.

(ii) Since $\tilde{M}$ is a symmetric operator, this subspace is orthogonal to X_1.

(iii) We normalize the vectors of this subspace. So, X_3 is given by

$$X_{3,\lambda}=\epsilon_\lambda\left[\frac{\beta C_E C_I}{TC}\right]^{1/2}\hbar\omega_\lambda[n_\lambda(n_\lambda+1)]^{1/2} , \tag{32}$$

with

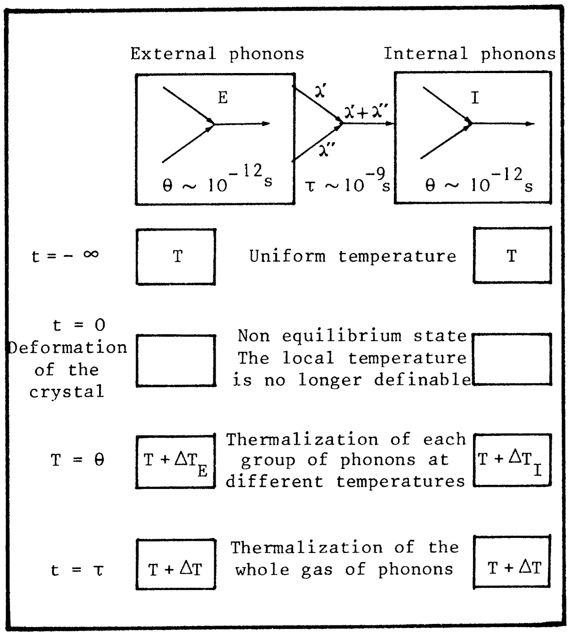


FIG. 2. Illustration of the behavior of phonons in a molecular crystal during the application of an elastic deformation.

$$\epsilon_\lambda = \begin{cases} \left[\dfrac{1}{C_E}\right], & \lambda \in E \\ \left[-\dfrac{1}{C_I}\right], & \lambda \in I\,. \end{cases} \tag{33}$$

Here C_E and C_I are the specific heats per unit volume associated with, respectively, the external and internal modes, so that $C_V = C_E + C_I$.

We may use the expression (32) of X_3 to derive the relation

$$\frac{\partial}{\partial t}\left[\frac{U_E}{C_E}-\frac{U_I}{C_I}\right]_{\mathrm{coll}} = -\frac{1}{\tau}\left[\frac{U_E}{C_E}-\frac{U_I}{C_I}\right]. \tag{34}$$

Physically this means that there is a slow transfer (with time τ) of energy between internal and external modes.

Now the degeneracy of the eigensubspace G associated with $-1/\Theta$ is $\mathcal{N}-2$. Then, with the help of relations (26) and (32) we get the following expression for α:

$$\alpha = \frac{C_V T}{2\rho s^3}\left[\langle\gamma^{(2)}\rangle - \langle\gamma\rangle^2 - \frac{C_I C_E}{C_V^2}(\langle\gamma\rangle_E - \langle\gamma\rangle_I)^2\right]\Omega^2\Theta + \frac{C_V T}{2\rho s^3}\frac{C_E C_I}{C_V^2}(\langle\gamma\rangle_E - \langle\gamma\rangle_I)^2\frac{\Omega^2\tau}{1+\Omega^2\tau^2} = \alpha_A + \alpha_R\,. \tag{35}$$

We have set

$$\langle\gamma\rangle_E = \frac{\beta}{TVC_E}\sum_{\lambda\in E}(\hbar\omega_\lambda)^2 n_\lambda(n_\lambda+1)\gamma_\lambda$$

and (36)

$$\langle\gamma\rangle_I = \frac{\beta}{TVC_I}\sum_{\lambda\in I}(\hbar\omega_\lambda)^2 n_\lambda(n_\lambda+1)\gamma_\lambda\,.$$

In this expression for α we have superposition of two terms where the first (α_A) is close to the classical term of Akhieser and the second (α_R) is a relaxation term we can now compare with Liebermann's.

VI. COMPARISON WITH PREVIOUS RELATIONS

A further approximation is necessary to make this comparison: We must neglect $\langle\gamma\rangle_I$ with regard to $\langle\gamma\rangle_E$. The existent experimental data on Grüneisen parameters in molecular crystals[26,27] bear out this approximation, which is in fact a direct consequence of the weakness of interactions between internal phonons and long-wavelength acoustic phonons. With such conditions, Eq. (35) becomes

$$\alpha_A = \frac{C_V T}{2\rho s^3}\left[\langle\gamma^{(2)}\rangle - \frac{C_V}{C_E}\langle\gamma\rangle^2\right]\Omega^2\Theta \tag{37}$$

and

$$\alpha_R = \frac{C_V T}{2\rho s^3}\frac{C_I}{C_E}\langle\gamma\rangle^2\frac{\Omega^2\tau}{1+\Omega^2\tau^2}\,. \tag{38}$$

We can express the generalized Grüneisen tensor $\langle\gamma_{ij}\rangle$ in terms of the specific heat at constant volume, the elastic constants C_{ijkl} of the harmonic theory, and the thermal expansion tensor β_{kl} using the following relation,[28] valid in the quasiharmonic approximation:

$$\langle\gamma\rangle = \langle\gamma_{ij}\rangle e_i K_j = \frac{1}{C_V}C_{ijkl}\beta_{kl}e_i K_j\,. \tag{39}$$

Thus we have

$$\alpha_R = \frac{T}{2\rho s^3}\frac{C_I}{C_V - C_I}\frac{(C_{ijkl}\beta_{kl}e_i K_j)^2}{C_V}\frac{\Omega^2\tau}{1+\Omega^2\tau^2}\,. \tag{40}$$

Using some thermodynamic relations, we can get other expressions of α_R from Eq. (40). For example, in isotropic and cubic symmetries, we have

$$\begin{gathered}\beta_{kl} = \tfrac{1}{3}\beta\delta_{kl}\,,\\ \frac{C_P - C_V}{C_V} = \frac{T\beta^2 B_S}{C_P}\,,\\ B_S = \tfrac{1}{3}(C_{11}^S + 2C_{12}^S)\,.\end{gathered} \tag{41}$$

Here β is the cubic thermal expansion coefficient, B_S is the adiabatic bulk modulus, C_{11}^S and C_{12}^S are the adiabatic second-order elastic constants in Voigt notation. Within our approximation the harmonic values of the elastic constants in Eq. (40) can be replaced by their isothermal values so that, in isotropic and cubic symmetries, Eq. (40) becomes

$$\alpha_R = \frac{1}{2s}\frac{C_P - C_V}{C_P}\frac{C_I}{C_V - C_I} \times \frac{C_{11}^S + 2C_{12}^S}{3\rho s^2}(\vec{e}\cdot\vec{K})\frac{\Omega^2\tau}{1+\Omega^2\tau^2} \, . \tag{42}$$

If we compare Eq. (42) with formula (1) used by Liebermann and in most of the other papers in this field (whatever the symmetry of investigated crystals), we see that there is a slight difference due to the existence in relation (42) of the structure factor $(C_{11}^S + 2C_{12}^S)/3\rho s^2$ which results from the actual nature of the solid state. It can be shown that, with some approximations, this relation is very close to that used by Danielmeyer[9] for the isotropic symmetry, but the extension by Victor and Beyer[13] of Danielmeyer's approach for lower symmetries is questionable. Moreover, it is impossible for symmetries lower than cubic to introduce in a natural way the quantity $(C_P - C_V)/C_P$ in the expression of α. However, instead of the relations (41) we may use the thermodynamic relation

$$C_{ijkl}^S - C_{ijkl}^T = \frac{T}{C_V}\sum_{mnrs} C_{ijmn}^T C_{klrs}^T \beta_{mn}\beta_{rs} \, , \tag{43}$$

which leads to our final expression for α valid for any symmetry,

$$\alpha = \frac{1}{2s}\frac{C_I}{C_E}\frac{C_{ijkl}^S - C_{ijkl}^T}{\rho s^2} e_i e_k K_j K_l \frac{\Omega^2\tau}{1+\Omega^2\tau^2} \cong \frac{\Omega}{s}\frac{C_I}{C_E}\frac{s^S - s^T}{s}\frac{\Omega\tau}{1+\Omega^2\tau^2} \, . \tag{44}$$

Here we have again replaced the harmonic values C_{ijkl} of the elastic constants by their isothermal values C_{ijkl}^T. This attenuation is related to a dispersion of the ultrasonic velocity given by

$$\frac{s - s_0}{s_0} \cong \frac{C_I}{C_E}\frac{s^S - s^T}{s}\frac{\Omega^2\tau^2}{1+\Omega^2\tau^2} \, . \tag{45}$$

It can be noted that Eqs. (38), (40), or (44) lead to a new qualitative fact which cannot be predicted by Eq. (1): Transverse waves which propagate in low symmetry crystals along what Borgnis[29] has termed "specific directions" can give rise to a molecular relaxation.

In the experimental field, the analysis of the curves giving α/Ω in terms of Ω brings two independent pieces of information about the relaxation: The magnitude of the maximum of these curves is linked with the coefficient of the term $\Omega^2\tau/(1+\Omega^2\tau^2)$ in Eqs. (1), (40), or (42), while its abscissa allows the determination of τ. To see whether the expression of α derived in this paper brings an improvement compared with those used previously, we have fitted recent experimental results[17,18] obtained along the fourfold and twofold axes of the isomorphous cubic crystals of strontium, barium, and lead nitrates, with the help of relations (1) and (42) to get "experimental" values of C_I', the heat capacity per mole associated with internal modes. As the internal vibrations of the ionic molecule $(NO_3)_2^{2-}$ are quite unaffected by lattice effects we must get the same values of C_I' not only for the two axes investigated in a same compound, but also for the entire set of experiments. The results listed in Table I show that formula (1) used by Liebermann leads to a large scatter of the values of C_I' of about 15%, which is reduced to less than 1% with relation (42), while the average value of C_I' increases from 17 to 20 J/mol K. This value may be compared with a theoretical evaluation of C_I' equal to 22 J/mol K deduced from infrared and Raman scattering data. Thus on this set of experimental results the relation between α and τ derived in this paper provides a better fit for the coefficient of the relaxation term $\Omega^2\tau/(1+\Omega^2\tau^2)$ than those used previously.

VII. INFLUENCE OF ANISOTROPY

An important aspect of the analysis is that both relations (1) and (42) assume that the relaxation spectrum is reduced to a single relaxation time, which thus must be the same whatever the direction of propagation of the ultrasonic wave. Now in two papers an anisotropy of τ has been reported,[13–18] and we will examine this occurrence in

TABLE I. Comparison of fits of experimental results (Ref. 18) realized by the means of our theory and that of Liebermann's.

Substance	Anisotropy	C_I'[a] (J/mol K)	C_I'[b] (J/mol K)
$Sr(NO_3)_2$	[100]	19.9	17.2
	[110]	19.8	14.6
$Ba(NO_3)_2$	[100]	20.6	19.9
	[110]	19.7	16.9
$Pb(NO_3)_2$	[100]	19.8	18.3
	[110]	19.9	15.8

[a] Experimental value of the heat capacity per mole deduced from the theory derived in this paper [Eq. (42)].

[b] Experimental value of C_I' deduced from Liebermann's theory [Eq. (1)].

this section.

To explain this anisotropy Victor and Beyer[13] have suggested the existence of multiple relaxation times τ_i ($i=3,\ldots,p$). However, relation (26) shows that these times are linked with the eigenvalues $-1/\tau_i$ of the collision operator, which are intrinsic properties of the crystal, so that the relaxation spectrum cannot be affected by anisotropy. Now the shift of the maxima of the curves giving α/Ω vs Ω due to the changes of the direction of propagation can only be explained by a strong influence of anisotropy on the respective magnitudes of the different relaxations τ_i. Nevertheless, we will show that under approximations weaker than those leading to Eq. (40) these magnitudes must stay proportional to one another for any measurements in the same compound.

We always distinguish two groups of phonons:

(i) On the one hand, there are phonons which participate in establishing a local equilibrium in a fast time Θ. For this group of phonons (we again write $\lambda\in E$) there is always conservation of the energy within the assumption $\theta/\tau_i << 1$.

(ii) On the other hand, there are phonons ($\lambda\in I$) which are not thermalized with times $\sim\Theta$. These phonons clearly have only weak interactions with acoustic phonons, and we assume that their Grüneisen parameters are negligible.

Under these conditions we have for $i>2$ and $\lambda\in E$

$$X_{i,\lambda}=\mu_i\hbar\omega_\lambda\left[\frac{\beta}{TC}n_\lambda(n_\lambda+1)\right]^{1/2}, \qquad (46)$$

where μ_i are normalizing factors which depend on intrinsic properties of the collision operator and thus are independent of the direction of propagation of the ultrasonic wave. So for $i>2$, we have

$$(X_i\cdot\tilde{\gamma})_F=(X_i\cdot\tilde{\gamma})_E=\sum_{\lambda\in E}X_{i,\lambda}\tilde{\gamma}_\lambda=\mu_i(\beta TC)^{1/2}\langle\gamma\rangle\,. \qquad (47)$$

Thus Eq. (26) gives

$$\alpha=\alpha_A+\alpha_R$$

with

$$\alpha_R=\frac{C_VT}{2\rho s^3}\langle\gamma\rangle^2\sum_{i=3}^{p}\mu_i^2\frac{\Omega^2\tau_i}{1+\Omega^2\tau_i^2}\,. \qquad (48)$$

In the expression above we see that anisotropy cannot act on the term

$$\sum_{i=3}^{p}\mu_i^2\frac{\Omega^2\tau_i}{1+\Omega^2\tau_i^2}\,,$$

but only on its coefficient through the term $\langle\gamma\rangle^2/s^3$ (within the approximation $\langle\gamma\rangle_I << \langle\gamma\rangle_E$). Moreover, this property has been shown even though we no longer have assumed the thermalization of "internal" phonons and thus we may expect that it remains valid for a large range of behavior of the "internal" phonons.

VIII. CONCLUSION

The consequences of the approach developed in this paper are the following.

The possibility of discussing the ultrasonic attenuation for the whole family of dielectric crystals within a single scheme whether these crystals are "hard" or molecular.

The formulation of the actual approximations (at a microscopic level) which support Liebermann's proposition.

The derivation of an expression of the ultrasonic absorption coefficient in molecular crystals which is different from that used in the previous works of this field and which leads to a closer fit in the analysis of some experimental results.

The discussion of the influence of anisotropy on the molecular relaxation where we have shown that under rather general conditions, anisotropy mainly acts on the magnitude of the ultrasonic absorption but not on its frequency dependence.

It would now be very interesting to go back to Liebermann's approach about relaxation times with the support of modern analysis of the anharmonicity in molecular crystals, which might lead to good predictions about the order of magnitude of these times and their dependence on parameters such as temperature, pressure, etc.

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APPENDIX

In this appendix we outline a derivation of the expression of α under the assumptions made in Sec. V but when the group velocity of phonons is taken into account. Now X_1, X_3, and G are no longer the eigensubspaces of $\hat{M}$ when the term $i\Omega\xi$ is kept in definition (24) of $\hat{M}$ and thus the expression of α cannot be obtained by a mere expansion of Eq. (25).

X_2 being a normalized vector of G parallel to the projection of $\tilde{\gamma}$ on G, we make the following definitions:

$$Z_i=\hat{M}(X_i)=Y_i+\sum_{k=1}^{3}\hat{m}_{ik}X_k\ ,\qquad Y_i\in G\ ,\quad \forall i=1,3\ . \tag{A1}$$

With these notations we have

$$\alpha=-\frac{\Omega}{2\rho Vs^3}\frac{1}{\beta}\mathrm{Re}\left[\sum_{i,k}(X_i\cdot\tilde{\gamma})_F(X_k\cdot\tilde{\gamma})_F\hat{m}_{ik}\right]\ , \tag{A2}$$

and now we must determine the term $\hat{m}_{ik}$. Using definition (24) of $\hat{M}$ we may obtain from (A1) the relation

$$X_i=\hat{M}^{-1}(Z_i)=-\frac{1}{\Omega\Theta}[1+i\Omega\Theta(I-\xi)](Z_i)+\sum_{k=1}^{3}\frac{\nu_2-\nu_k}{\Omega}\hat{m}_{ik}X_k\ , \tag{A3}$$

where

$$\nu_1=0\ ,\quad \nu_2=\frac{1}{\Theta}\ ,\quad \nu_3=\frac{1}{\tau}\ . \tag{A4}$$

If we let

$$A=-\frac{1}{\Omega\Theta}[1+i\Omega\Theta(I-\xi)]\ , \tag{A5}$$

then (A3) may be written in the form

$$A^{-1}(X_i)=Z_i+\sum_{k=1}^{3}\frac{\nu_2-\nu_k}{\Omega}\hat{m}_{ik}A^{-1}(X_k)\ . \tag{A6}$$

If we multiply both sides of Eq. (A6) by X_j, we find

$$a_{ji}=\sum_{k=1}^{3}\hat{m}_{ik}\left[\frac{1}{\Omega\Theta}(1-\Theta\nu_k)a_{jk}+\delta_{jk}\right]=\sum_{k=1}^{3}\hat{m}_{ik}b_{kj}\ , \tag{A7}$$

where

$$a_{ji}=(X_j\cdot A^{-1}(X_i))_F=a_{ij}\ ,\qquad b_{kj}=\frac{1}{\Omega\Theta}(1-\Theta\nu_k)a_{jk}+\delta_{jk}\ . \tag{A8}$$

Here $\hat{m}_{ik}$, a_{ji}, and b_{kj} may be considered as elements of three matrices (3×3) denoted $\hat{m}$, a, and b. Then we have from (A7)

$$\hat{m}=ab^{-1}\ . \tag{A9}$$

The next step of this derivation is to obtain an explicit expression of the elements a_{ij}. With the help of the definition (A5) we can write

$$A_{\lambda\lambda'}^{-1}=-\frac{\Omega\Theta\delta_{\lambda\lambda'}}{1+i\Omega\Theta(1-\xi_{\lambda\lambda})}\ . \tag{A10}$$

If we assume that we are in the hydrodynamical region ($\Omega\Theta<<1$) we can make an expansion of $A_{\lambda\lambda'}^{-1}$ in terms of $\Omega\Theta$, and we find

$$a_{ij}=(X_i\cdot A^{-1}(X_j))_F=-\Omega\Theta[\delta_{ij}(1-\Omega\Theta-\Omega^2\Theta^2)-\Omega^2\Theta^2\xi_{ij}^2+O(\Omega^3\Theta^3)]\ , \tag{A11}$$

where

$$\xi_{ij}^2=\sum_{\lambda\in F}\left[\frac{\vec{v}_\lambda\cdot\vec{K}}{s}\right]^2X_{i,\lambda}X_{j,\lambda}\ . \tag{A12}$$

The operator ξ does not give a first-order term in $\Omega\Theta$ in the expansion of $a_{ij}/\Omega\Theta$ because the group velocities $\vec{v}_\lambda$ and $\vec{v}_{-\lambda}$ cancel out while the components $X_{i,\lambda}$ and $X_{i,-\lambda}$ are equal.

Now with the help of Eqs. (A2), (A7), (A9), and (A11), and after some tedious but straightforward calculations it can be shown that α may be written in the form

$$\alpha=\alpha_A+\alpha_R+\alpha_T\ , \tag{A13}$$

where α_A and α_R have already been defined by Eq. (35), and α_T is the attenuation due to thermal conduction between the compressed and rarefied regions and is given by

$$\alpha_T=\frac{C_V T}{2\rho s^3}\Omega^2\Theta\left[\langle\gamma\rangle^2\langle\xi^2\rangle+\frac{C_E C_I}{C_V^2}\langle\gamma\rangle(\langle\gamma\rangle_E-\langle\gamma\rangle_I)(\langle\xi^2\rangle_E-\langle\xi^2\rangle_I)\left[2-\frac{\Theta}{\tau}\right]\frac{\Omega^2\tau^2}{1+\Omega^2\tau^2}\right.$$
$$\left.-\frac{C_E C_I}{C_V^2}(\langle\gamma\rangle_E-\langle\gamma\rangle_I)^2\left[\frac{C_I}{C_V}\langle\xi_E^2\rangle+\frac{C_E}{C_V}\langle\xi_I^2\rangle\right]\frac{\Omega^2\tau^2(1-\Omega^2\tau^2)}{(1+\Omega^2\tau^2)^2}\right]. \tag{A14}$$

We have set

$$\langle\xi^2\rangle=\frac{\beta}{TC}\sum_{\lambda\in F}(\hbar\omega_\lambda)^2 n_\lambda(n_\lambda+1)\xi_{\lambda\lambda}^2\,, \tag{A15}$$

and $\langle\xi^2\rangle_E$ and $\langle\xi^2\rangle_I$ are defined in the same way. Since the internal modes are quite unaffected by lattice effects we may neglect $\langle\gamma\rangle_I$ and $\langle\xi^2\rangle_I$ in Eq. (A14) to obtain a slightly simplified expression of α_T:

$$\alpha_T=\frac{C_V T}{2\rho s^3}\langle\gamma\rangle^2\langle\xi^2\rangle\Omega^2\Theta\left[1+\frac{C_I}{C_E}\left[2-\frac{\Theta}{\tau}\right]\frac{\Omega^2\tau^2}{1+\Omega^2\tau^2}-\left[\frac{C_I}{C_E}\right]^2\frac{\Omega^2\tau^2(1-\Omega^2\tau^2)}{(1+\Omega^2\tau^2)^2}\right]. \tag{A16}$$

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