the angular positions of the principal maxima with respect to the direct beam were predicted to remain approximately fixed with respect to the incident glancing (for small angles) and to be $\Delta = n\lambda/d$. This prediction was verified for incident glancing angles up to 13 664 sec. A similarity between the pattern produced by optical diffraction from a plane grating containing only a few lines and the interference structure of the nonspecularly scattered radiation from barium stearate multilayer films was also noted.

Much investigation of the structure in the scattered radiation still remains to be done. In particular, a detailed investigation of the intensities of the various interference fringes should be made with the hope of determining the form factor for the scattered radiation. The origin of the doublet structure should be investigated as should the interference pattern produced at incident glancing angles less than the critical angle for the film.

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Evidence for a Considerable Nonlinear Dipole Absorption in Gallium Arsenide*

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A comparison is made of the infrared lattice absorption spectra of Ge and GaAs. For this purpose an approximate damping function is derived for GaAs. The comparison of the damping functions shows that both the nonlinear dipole moment and the anharmonicity should be important for the absorption of GaAs in the two-phonon and three-phonon summation bands. The matrix elements for these two mechanisms are found to have nearly the same order of magnitude. In the absorption coefficient and in the imaginary part of the dielectric constant, the anharmonicity in connection with the infrared-active lattice mode dominates at frequencies near the resonance frequency ω_0, while the nonlinear dipole moment dominates in the three-phonon summation-band region where $(\omega^2/\omega_0^2 - 1) \gg 1$.

1. INTRODUCTION

THE infrared absorption of ionic crystals may be interpreted in terms of an infrared-active lattice mode (dispersion oscillator) in connection with the anharmonicity of the lattice potential on the one hand and in terms of the nonlinear dipole moment on the other hand. Several authors assumed the former mechanism to be dominant in alkali halides and explained the infrared absorption of these materials by this mechanism[1–4] whereas the absorption in homopolar crystals as diamond, Si and Ge is due to the latter only.[5] Some recent papers have already considered the relative importance of the nonlinear dipole moment in ionic crystals.[6–12] By comparing the integrated absorption in the two optical-phonon summation bands (LO+LO, TO+LO and TO+TO, where LO=longitudinal optic and TO=transverse optic) of GaP and Ge, Kleinman and Spitzer[6,7] deduced that the nonlinear dipole-moment absorption in GaP was smaller by an order of magnitude than the absorption due to the anharmonicity. However, Szigeti[9] pointed out from theoretical considerations that this conclusion should not be true and that the nonlinear dipole moment should contribute a considerable amount to the absorption in the two-phonon summation bands of ionic crystals, even in the case of alkali halides.

2. THEORETICAL CONSIDERATIONS

In this paper the infrared absorption spectrum of GaAs will be compared with that of Ge in the two-

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[†] On leave of absence from Physikalisches Institut der Universität Freiburg i Br., Germany, where the work summarized in this paper was begun.

[1] H. Bilz, L. Genzel and H. Happ, Z. Physik **160**, 535 (1960).

[2] H. Bilz and L. Genzel, Z. Physik **169**, 53 (1962).

[3] V. V. Mitskewich, Fiz. Tverd. Tela **3**, 3036 (1961) [English transl.: Soviet Phys.—Solid State **3**, 2211 (1962)].

[4] V. S. Vinogradov, Fiz. Tverd. Tela **4**, 712, (1962) [English transl.: Soviet Phys.—Solid State **4**, 519 (1962)].

[5] M. Lax and E. Burstein, Phys. Rev. **97**, 39 (1955).

[6] D. A. Kleinman and W. G. Spitzer, Phys. Rev. **118**, 110 (1960).

[7] D. A. Kleinman, Phys. Rev. **118**, 118 (1960).

[8] V. V. Mitskevich, Fiz. Tverd. Tela **4**, 3035 (1962) [English transl.: Soviet Phys.—Solid State **4**, 2224 (1963)].

[9] B. Szigeti, Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963 (Pergamon Press, Inc., New York, to be published).

[10] R. A. Cowley, Advan. Phys. **12**, 421 (1963).

[11] H. Hartmann and J. L. Birman, Bull. Am. Phys. Soc. **9**, 236 (1964).

[12] R. Wehner, thesis, Freiburg, Germany, 1964 (unpublished).

phonon and three-phonon summation-band regions with respect to the relative importance of the nonlinear dipole-moment absorption. For this purpose a formula will be used which was derived by Szigeti[13] for the imaginary part ϵ'' of the dielectric constant at frequencies sufficiently far away from the eigenfrequency:

$$\epsilon''=a\left[\delta_{\beta^2}-\frac{2\delta_{\alpha\beta}}{1-\Omega^2}+\frac{\delta_{\alpha^2}}{(1-\Omega^2)^2}\right] \tag{1}$$

with

$$\delta_{\alpha^2}=\sum_{ij}\oint_{\omega=\mathrm{const}} f_{ij}\frac{\alpha_0{}^2b_{0ij}{}^2}{\omega_0{}^4}d\sigma\,,$$

$$\delta_{\alpha\beta}=\sum_{ij}\oint_{\omega=\mathrm{const}} f_{ij}\frac{\alpha_0b_{0ij}\beta_{ij}}{\omega_0{}^2}d\sigma\,,$$

$$\delta_{\beta^2}=\sum_{ij}\oint_{\omega=\mathrm{const}} f_{ij}\beta_{ij}{}^2d\sigma. \tag{1a}$$

In Eq. (1) and (1a), a is a constant factor, ω the frequency of incident light, and $\Omega=\omega/\omega_0$ the frequency reduced by the eigenfrequency of the dispersion oscillator for GaAs and by the Raman frequency for Ge. The f_{ij} terms contain the thermal averages of the phonon quantum numbers and are functions of the temperature, the phonon frequencies and of a density factor which yields the combined density of states after integration in reciprocal space. The indices i and j refer to phonon branches i and j. α_0 and β_{ij} are the coefficients of the first- and second-order dipole moment with respect to the normal coordinates. The b_{0ij} are the coefficients of the cubic terms in the lattice potential.[14] $d\sigma$ is a surface element of the surface $\omega=\omega_i+\omega_j=\mathrm{const}$ in $\mathbf{q}$ space.

In this investigation phonon difference processes will be neglected as the summation processes are more important at frequencies $\Omega>1$. This frequency region is of main interest here for reasons of the strongly varying frequency factors in Eq. (1). From Eq. (1) it is seen also that the temperature dependence as given by the functions f_{ij} is the same for the two absorption mechanisms. Measurements of the absorption at various temperatures exhibit no information about this problem. However, such information should be obtained by comparing two materials with similar phonon spectra, i.e., a polar and a nonpolar crystal with similar lattice modes.

The expressions (1a) are the frequency-dependent damping functions. If for an ionic crystal like LiF the nonlinear dipole moment is assumed to be negligible, the remaining damping function δ_{α^2} may be calculated from the experimentally determined values of ϵ'' (cf. Refs. 2, 8, 12).

$$\delta_{\alpha^2}=\frac{\epsilon''}{\epsilon_0-\epsilon_\infty}(1-\Omega^2)^2\,,\quad\text{with}\quad a=\epsilon_0-\epsilon_\infty. \tag{2}$$

For homopolar crystals the linear dipole moment (α_0) vanishes and the only damping function δ_{β^2} is proportional to ϵ'' without any explicit frequency factor

$$\delta_{\beta^2}\sim\epsilon''. \tag{3}$$

When we have to take into account for a weakly ionic crystal both the anharmonicity and the nonlinear dipole moment, we are unable to calculate the three damping functions (1a) using only the experimental information of ϵ''. From mathematical arguments it can be shown that

$$(\delta_{\alpha\beta})^2<\delta_{\alpha^2}\delta_{\beta^2} \tag{4}$$

if the ratio $c_{ij}=\beta_{ij}\omega_0{}^2/\alpha_0b_{0ij}$ of the nonlinear dipole moment and the anharmonic effects depends on wave vector $\mathbf{q}$ and on branches i and j. If $c_{ij}=c=\mathrm{const}$, then the following conditions holds instead of (4)

$$(\delta_{\alpha\beta})^2=\delta_{\alpha^2}\delta_{\beta^2}. \tag{5}$$

In the case $c=\mathrm{const}$ the problem arises that ϵ'' may vanish in spite of $\delta_{\alpha^2}\neq0$, $\delta_{\alpha\beta}\neq0$, and $\delta_{\beta^2}\neq0$ (cf. Ref. 9). Equation (1) yields $\epsilon''=0$ at frequencies

$$\Omega^2=1-\frac{\delta_{\alpha\beta}}{\delta_{\beta^2}}\pm\frac{1}{\delta_{\beta^2}}[(\delta_{\alpha\beta})^2-\delta_{\alpha^2}\delta_{\beta^2}]^{1/2}. \tag{6}$$

In the case of $(\delta_{\alpha\beta})^2<\delta_{\alpha^2}\delta_{\beta^2}$ or $c_{ij}=f(\mathbf{q},i,j)$ (cf. Eq. 4), the condition (6) cannot be fulfilled with real $\Omega>0$ and thus $\epsilon''\neq0$ if δ_{α^2}, $\delta_{\alpha\beta}$, $\delta_{\beta^2}\neq0$. However, in the case of $(\delta_{\alpha\beta})^2=\delta_{\alpha^2}\delta_{\beta^2}$ or $c_{ij}=c=\mathrm{const}$ (cf. Eq. 5) it follows from Eq. (6) $\epsilon''=0$ at the frequency $\Omega^2=1-\delta_{\alpha\beta}/\delta_{\beta^2}=1-1/c$. Since the experimentally determined imaginary part of the dielectric constant does not vanish in the spectral region under consideration, the assumption $c=\mathrm{const}$ may be a crude, but for a first approximation, helpful simplification. However, the values of c should be limited to the range $0\leqq c\leqq1$.

Though Eq. (1) has been derived for two phonon processes, it may be extended to the three-phonon region which starts at $\Omega\geqq2$ (Ge) or $\Omega\geqq2(\epsilon_0/\epsilon_\infty)^{1/2}$

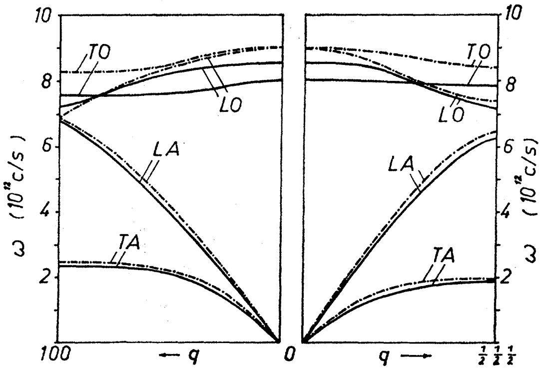

FIG. 1. Phonon frequencies ω versus wave vector q of Ge (—·—) and GaAs (——) for the directions (100) and (111) as measured by neutron spectrometry. The data were taken from Ref. 15 (Ge) and Ref. 17 (GaAs).

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[13] B. Szigeti, Proc. Roy. Soc. (London) **A258**, 377 (1960).

[14] For details and for the denotation see Ref. 13.

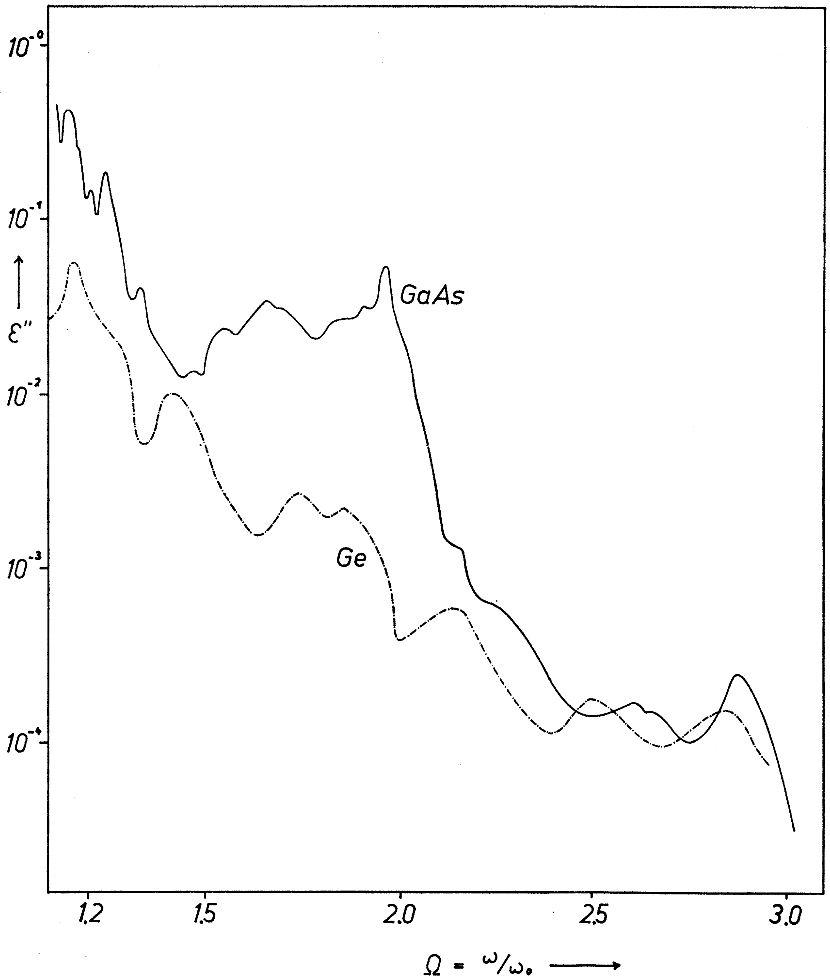

FIG. 2. The imaginary part ϵ'' of the dielectric constant for Ge (—·—) and GaAs (——) versus reduced frequency Ω in the two-phonon and three-phonon summation-band region. The Raman frequency of Ge is $\omega_0 = 9.0 \times 10^{12}$ cps and the eigenfrequency of GaAs is $\omega_0 = 8.02 \times 10^{12}$ cps. ϵ'' was calculated from the absorption coefficients of Ge (Refs. 18, 19) and GaAs (Refs. 20, 21).

(GaAs). Here the expressions (1a) vanish and we have to consider the next-higher-order terms in the dipole moment and the lattice potential. Equation (1) will hold also in the three-phonon summation-band region with damping functions δ_{α^2} containing essentially the contribution of the fourth-order lattice potential connected with the linear dipole moment, δ_{β^2} containing essentially the contributions of the third-order dipole moment and $\delta_{\alpha\beta}$ with the interference of both absorption mechanisms. Furthermore, these damping functions are assumed to have the same mathematical structure as those given explicitly in Eq. (1a) and consequently the conclusions (4)–(6) would be correct in this case but the accuracy of this assumption cannot be surveyed here and is still open to discussion.

3. COMPARISON OF THE ABSORPTION OF Ge AND GaAs

For the absorption spectra, Ge and GaAs appear to be particularly suitable materials to be compared, as they have a similar crystal structure. The atomic masses and the Debye temperatures are nearly the same and the phonon frequencies determined by neutron spectrometry[15–17] agree within 10% (cf. Fig. 1). However, there are differences between the two materials as GaAs, in contrast to Ge, has no center of symmetry but has a dispersion oscillator. The former difference causes some deviations in the selection rules for the summation bands and the latter a different frequency dependence of ϵ'' in that region where the influence of the anharmonicity via dispersion oscillator dominates. In order to eliminate the resonance denominator $(1-\Omega^2)$ due to the dispersion oscillator, it is useful to compare the damping functions of Ge and GaAs. Their frequency dependence is mainly governed by the combined density of states and the phonon critical points.

The room-temperature absorption coefficients of

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[15] B. N. Brockhouse and P. K. Jyengar, Phys. Rev. **111**, 747 (1958).

[16] A. Ghose, H. Palevsky, D. J. Hughes, J. Pelah, and C. M. Eisenhauer, Phys. Rev. **113**, 49 (1959).

[17] J. L. T. Waugh and G. Dolling, Phys. Rev. **132**, 2410 (1963).

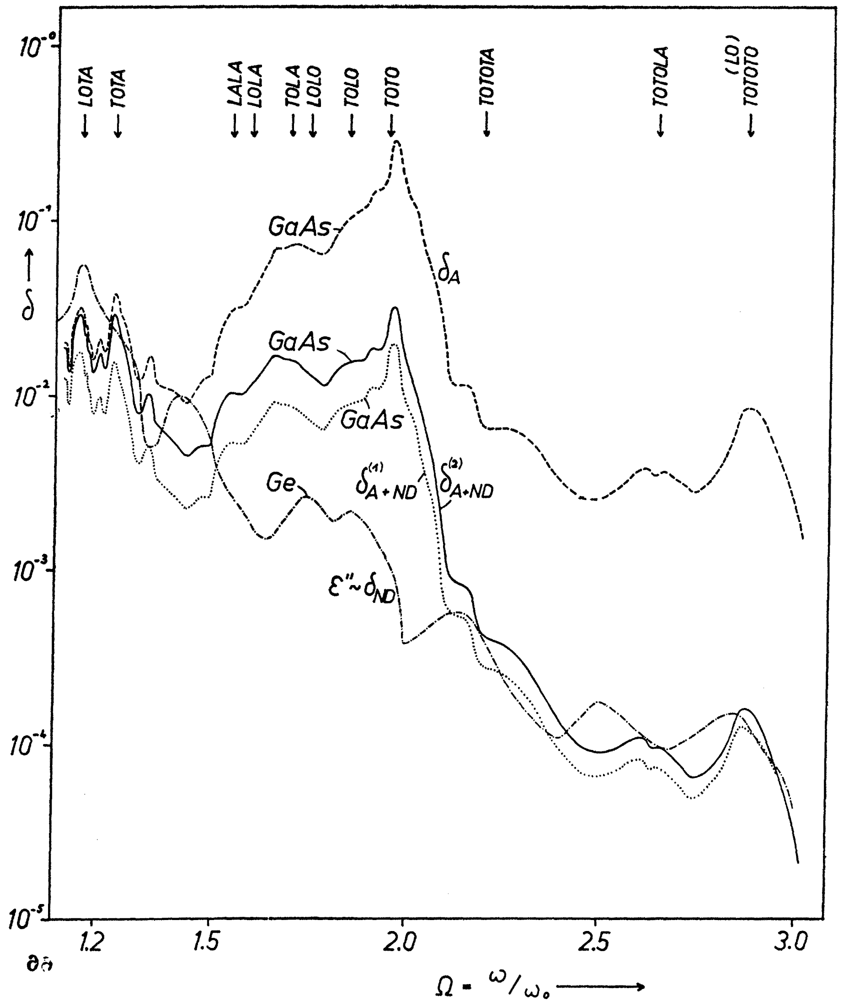

FIG. 3. Approximate damping functions of GaAs versus reduced frequency Ω: δ_A(– – –) calculated by means of Eq. (7) with $c=0$, $\delta_{A+ND}^{(1)}$ (····) calculated by means of Eq. (7) with $c=1$ and $\delta_{A+ND}^{(2)}$ (——) calculated by means of Eq. (8) with $d^2=1$. And, for comparison: $\epsilon''\sim\delta_{ND}$ (–·–) of Ge.

Ge (Refs. 18, 19) and GaAs (Refs. 20, 21) measured in the infrared spectral region were converted to $\epsilon''=2nk$ (cf. Fig. 2) by using $n=4.00$[22,23] for Ge. The refractive index of GaAs was computed by means of a classical dispersion formula with $\epsilon_0=12.4$,[17,24] $\epsilon_\infty=10.9$,[25] and $\nu_0=267$ cm^{-1}.[17,24] While the damping function of Ge is equal to ϵ'', apart from a constant factor, the damping function of GaAs can be calculated only with some simplifying assumptions. In default of other possibilities, it is assumed for a rough approximation that the ratio $c=\delta_{\alpha\beta}/\delta_{\alpha^2}=\delta_{\beta^2}/\delta_{\alpha\beta}$ of the nonlinear dipole moment and the anharmonic effects is a constant and is the same for two-phonon and three-phonon summation processes. Then $\delta=\delta_{\alpha^2}=(1/c)\delta_{\alpha\beta}=(1/c^2)\delta_{\beta^2}$ may be calculated from ϵ'':

$$\delta=\frac{\epsilon''}{\epsilon_0-\epsilon_\infty}(1-\Omega^2)^2[c(1-\Omega^2)-1]^{-2}, \qquad (7)$$

where $a=\epsilon_0-\epsilon_\infty$. As c probably would be frequency-dependent in a more accurate treatment, it ought to be understood as an average over the entire frequency region under consideration, and it will be determined by comparing the damping functions of Ge and GaAs. In view of the ratio c, the three δ's of GaAs are assumed to be proportional. Therefore this comparison is essentially a comparison of the nonlinear dipole moment (δ_{β^2}) of Ge and GaAs apart from constant factors. For that purpose δ of GaAs was computed by means of Eq. (7) for various values of c in the range $0\leqq c\leqq 1$. For the two limiting values $c=0$ and $c=1$, δ is shown in Fig. 3 (curve δ_A and $\delta_{A+ND}^{(1)}$). Near the resonance frequency ($\Omega\approx 1.2$) δ does not vary perceptibly for different values of c because here ϵ'' obviously is dominated by an-

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[18] G. Wimeral, thesis, Michigan, 1953 (unpublished; for the results, see Ref. 15).

[19] R. J. Collins and H. Y. Fan, Phys. Rev. **93**, 674 (1954).

[20] S. J. Fray, F. A. Johnson, J. E. Quarrington, and N. Williams, Proc. Phys. Soc. **77**, 215 (1961).

[21] W. Cochran, S. J. Fray, F. A. Johnson, J. E. Quarrington, and N. Williams, J. Appl. Phys. Suppl. **32**, 2102 (1961).

[22] A. C. Baynham, A. F. Gibson, and J. W. Granville, Proc. Phys. Soc. **75**, 306 (1960).

[23] C. D. Salzberg, and J. Villa, J. Opt. Soc. Am. **48**, 579 (1958).

[24] G. Picus, E. Burstein, B. W. Henvis, and M. Hass, J. Phys. Chem. Solids **8**, 282 (1959).

[25] B. K. Hambleton, C. Hilsum, and B. R. Holeman, Proc. Phys. Soc. **77**, 1147 (1961).

harmonic effects. Away from the resonance frequency ($\Omega > 1.7$), δ varies drastically as a function of c owing to the fact that the influence of δ_{α^2}, $\delta_{\alpha\beta}$, and δ_{β^2} on ϵ'' is governed by different explicit frequency factors (cf. Eq. 1).

In the case $c=0$, the nonlinear dipole moment is neglected and δ of GaAs is found to increase with increasing frequency by an order of magnitude in the two-phonon region ($1 \leqq \Omega \leqq 2$) and to have nearly the same value in the three-phonon region ($2 \leqq \Omega \leqq 3$) as at the (TO+TA) summation band ($\Omega \approx 1.2$) (cf. Fig. 3, curve δ_A). However, in the three-phonon region, δ is expected to be less than δ at such a prominent two-phonon peak as TO+TA by at least an order of magnitude. The comparison of δ for GaAs to $\delta \sim \epsilon''$ for Ge shows on the average a systematic increase of the ratio $\delta(\text{GaAs})/\delta(\text{Ge})$, which is ascribed to an overestimation of the anharmonic effects due to the factor $(1-\Omega^2)$ connected with them.

In the case $c=1$ ($\delta_{\alpha^2} \approx \delta_{\alpha\beta} \approx \delta_{\beta^2}$), δ for GaAs has the same order of magnitude as that for Ge in the regions $1.2 \leqq \Omega \leqq 1.5$ and $2 \leqq \Omega \leqq 3$ (cf. Fig. 3, curve $\delta_{A+ND}^{(1)}$). However, in the region $1.5 \leqq \Omega \leqq 2$ there is a considerable difference, and this will be discussed later. On the whole, the agreement between GaAs and Ge is better for $c=1$ than for $c=0$, and there is no systematic frequency dependence of the ratio $\delta(\text{GaAs})/\delta(\text{Ge})$ for $c=1$. For intermediate values of c, e.g., $c=10^{-1}$, there is again a systematic increase of the ratio mentioned above. Thus values for c of the order 1 appear to be the most reasonable fit.

In contrast to the approximation with $(\delta_{\alpha\beta})^2 = \delta_{\alpha^2}\delta_{\beta^2}$ or $c=\text{const}$ [cf. Eqs. (4) and (5)] in the preceding section, another approximation for the damping function of GaAs will be made presuming $(\delta_{\alpha\beta})^2 \ll \delta_{\alpha^2}\delta_{\beta^2}$, i.e., c is no longer a constant and the interference term $\delta_{\alpha\beta}$ is assumed to be small compared to δ_{α^2} and δ_{β^2}. Neglecting $\delta_{\alpha\beta}$ completely and putting $\delta = \delta_{\alpha^2} = (1/d^2)\delta_{\beta^2}$ with d^2 independent of frequency, the following formula enables us to evaluate a damping function of GaAs somewhat different from that given by Eq. (7):

$$\delta = \frac{\epsilon''}{\epsilon_0 - \epsilon_\infty}(1-\Omega^2)[d^2(1-\Omega^2)^2+1]^{-1}. \tag{8}$$

It should be noted that $d^2 = \delta_{\beta^2}/\delta_{\alpha^2}$ is a ratio of the damping functions but not of the coefficients β_{ij}, b_{0ij}, etc. Thus it may depend in general on the frequency but not on wave vector and branches i and j of the phonons. For this approach also, the best fit is obtained with d^2 values of order 1. In Fig. 3, δ is shown for $d^2=1$ denoted as $\delta_{A+ND}^{(2)}$. The agreement and the ratio of the damping functions for Ge and GaAs are essentially the same as for the former approach for $c=1$.

Another argument for $c \approx 1$ or $d^2 \approx 1$ is the fact that the experimentally measured values of ϵ'' for Ge and GaAs are equal in the three-phonon region apart from a slight shift of the peaks (cf. Fig. 2) and the absorption mechanisms are suggested to be the same for both materials in this region. If all three δ's of GaAs have the same order of magnitude, the denominator $(1-\Omega^2)$ diminishes the terms with δ_{α^2} and $\delta_{\alpha\beta}$ in Eq. (1) and ϵ'' is determined by δ_{β^2} in the three-phonon region.

4. CONCLUSION

From these considerations of the damping functions of Ge and GaAs, we may conclude that the nonlinear dipole moment cannot be neglected in the case of GaAs but on the average it has nearly the same order of magnitude as the effect of anharmonicity in connection with the dispersion oscillator. This statement agrees quite well with the theoretical results of Szigeti.[9] He defines

$$\frac{e^*-e}{e^*}\varphi_{ij} = \frac{\beta_{ij}{\omega_0}^2}{\alpha_0 b_{0ij}}(=c)$$

(cf. Eqs. 4 and 5a in Ref. 9) and finds φ_{ij} to be positive and of order 1 for alkali halides $[(e^*-e)/e^* \approx -(\frac{1}{3})]$. If this relation is applied to GaAs, it turns out $c \approx 1$ since $|(e^*-e)/e^*| \approx 1$ for compound semiconductors.

The discrepancy of Ge and GaAs in the region $1.5 \leqq \Omega \leqq 2$ found in this investigation may be partly due to the difference of the selection rules for the two materials and partly due to a larger second-order dipole-moment absorption in GaAs. For zincblende structure, overtones (LA+LA, TO+TO, LO+LO, where LA = longitudinal acoustic) are allowed in the two-phonon spectrum but unallowed for diamond structure.[26] In ionic crystals like GaAs the second-order dipole-moment results from two-atom interactions, whereas in homopolar crystals as Ge it results from three-atom interactions.[9] Thus the nonlinear dipole moment of GaAs may be larger.

Similar results were obtained for GaP by calculating approximative damping functions using Eq. (7) or (8) and by comparing them to Ge. These results are not given in detail because the absorption coefficient of GaP[6] has not been measured in the entire frequency region considered for the comparison.

The problem of the relative importance of the nonlinear dipole moment in GaAs was treated here under simplifying assumptions. A more accurate treatment would involve an explicit calculation of the three damping functions, using a force model (e.g., shell model) with parameters fitted to the phonon frequencies as determined by neutron spectroscopy.[17]

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[26] J. L. Birman, Phys. Rev. **131**, 1489 (1963).