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Phonon localization in glasses

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A universal but unexplained characteristic of glasses is the temperature-independent region or plateau in the thermal conductivity for temperatures 1–30 K. Examination of low-temperature thermal conductivity data for a wide variety of glasses indicates that the mean free path of the average thermal phonon becomes less than the phonon wavelength at temperatures in the vicinity of the plateau. Comparison with similar data in aggregates suggests that Ioffe-Regel localization of the vibrational modes occurs for phonons whose wavelength and mean free path are on the order of a structural correlation length of the material. Typical correlation lengths in glasses determined by this argument are 20–50 Å. The universal plateau in bulk glasses is therefore associated with phonon localization due to strong scattering from inhomogeneities on this length scale.

I. INTRODUCTION

Low-temperature studies over the past fifteen years have yielded a great deal of information on the structure and dynamics of glasses.[1] The universal thermal, electrical, and acoustical properties below 1 K have been traced to a broad distribution of intrinsic two-level tunneling systems (TS's). The typical glassy features *above* 1 K, however, are much less well understood. The thermal conductivity κ of glasses, for instance, generally exhibits a broad, temperature-independent plateau for $T \sim 1-30$ K, between the T^2 low-temperature behavior and an approximately linear behavior at high temperature. There have been many attempts to explain the plateau in terms of propagating thermal phonons, including elastic[2–5] and inelastic[6,7] scattering of phonons from TS's, Rayleigh scattering from density fluctuations[4,8–11] or phonon dispersion.[12] Nonpropagating vibrational modes have also been invoked. For example, they have been suggested as centers which scatter propagating phonons.[4] Alternatively, on the postulate that glasses are fractal, it has been proposed[13,14] that a band of fractons (the localized vibrations of a fractal object) is responsible for the plateau. Another very recent study[15] reveals a plateaulike feature in the thermal conductivity of powder aggregates which appears at a temperature that depends on the particle size. In particular, it occurs at a temperature for which the average thermal phonon wavelength λ is equal to the particle size (or the correlation length of the structure), which is also equal to the mean free path l. The equality of λ and l suggests that phonons in the vicinity of the plateau in aggregates are localized. This has prompted us to reexamine the thermal-conductivity data for a wide variety of glasses. Using the usual kinetic formula for κ and assuming thermal-phonon heat carriers at the lowest temperatures, we find a mean free path $l(\omega)$ which becomes shorter than the thermal phonon wavelength at a temperature near the upper end of the plateau. We therefore propose a picture in which phonon localization takes place for phonons with wavelength near some structural correlation length ξ, and we argue that this is intimately connected with the plateau.

The evidence presented here is for the Ioffe-Regel[16] condition $(kl \sim 1)$ being satisfied by phonons in glasses. Recent calculations[17] show that a mobility edge can occur for high-frequency phonons in a disordered medium of dimensionality greater than two, and it has been further suggested[18] that weak localization of phonons may be related to the plateau. Whether or not the situation can be described by Anderson localization[19,20] of phonons depends upon quantities such as the inelastic and elastic scattering lengths which have not yet been determined at the energies in question.[21,22]

II. EXPERIMENTAL RESULTS

The thermal conductivities of a wide variety of glasses are shown in Fig. 1. Glasses have been chosen for which sound-velocity measurements are also available.[4,23–25]

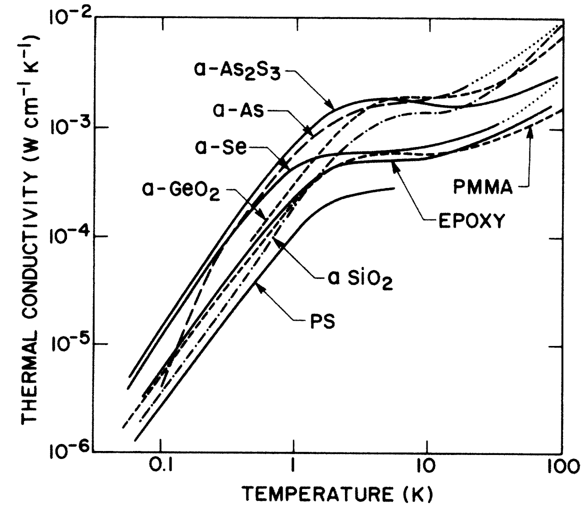

FIG. 1. Thermal conductivity of a-SiO$_2$ (Ref. 8), a-GeO$_2$ (Ref. 36), a-As$_2$S$_3$ (Refs. 7 and 23), a-As (Ref. 4), a-Se (Ref. 8), epikote epoxy (Ref. 24, sample N), and polymethylmethacrylate (PMMA) and polystyrene (PS) (Ref. 37).

The plateau is readily discernible for each glass, and the well-known remarkable similarity from glass to glass is exhibited. The similarity of the plateaus includes *a*-As which, however, is anomalous at temperatures *below* 1 K. It has been shown[4] that *a*-As has an unusually low density of TS's and that the low-temperature conductivity is dominated by scattering from a large number of voids in the sample.

It is usually assumed[1] that long-wavelength acoustic phonons are the dominant heat carriers at low temperatures and that one can calculate $\kappa(T)$ using the formula

$$\kappa(T)=(v/3)\int_0^{\omega_D}C(\omega,T)l(\omega)d\omega\ , \qquad (1)$$

where C is the heat capacity of the thermal carriers with cutoff frequency ω_D and average velocity v. This approach has been used successfully to account for not only the temperature dependence but also the absolute magnitude of κ. That is, $l(\omega)$ and v obtained from acoustic measurements can be inserted in Eq. (1) to obtain a conductivity that agrees with experiment.[26,27] For temperatures below 1 K, the assumption of propagating thermal phonons carrying the heat is therefore justified.

To reproduce the observed κ over the full temperature range of Fig. 1, we write[2,5,11,28]

$$l(\omega)=(l_t^{-1}+l_R^{-1})^{-1}+l_{\min}\ . \qquad (2)$$

l_t is the mean free path due to scattering from TS's:

$$l_t^{-1}=A(\hbar\omega/k_B)\tanh(\hbar\omega/2k_BT)$$
$$+(A/2)(k_B/\hbar\omega+B^{-1}T^{-3})^{-1}\ , \qquad (3)$$

where the two terms represent resonant scattering and relaxational absorption, respectively.

In terms of microscopic variables in the tunneling-system model, A and B are given by

$$A=\pi\tilde{n}\gamma^2k_B/\rho v^3\hbar \qquad (4)$$

and

$$B=\pi^2k_B^2\gamma^2/\rho\hbar^3v^5\ , \qquad (5)$$

where $\tilde{n}$ is the subset of tunneling states which are strongly coupled to phonons, γ is an average deformation potential, ρ is the mass density, and v is the average phonon velocity. A density of TS's is assumed to be constant. We have assumed that the low-temperature part of the plateau arises from Rayleigh scattering,

$$l_R^{-1}=D\hbar^4\omega^4/k_B^4\ , \qquad (6)$$

but we note[2,4] that this form is not unique, since any mechanism resulting in a very rapid decrease of l with ω would suffice. $l_{\min}$ is constant which is the usual lower limit on l to prevent it from becoming unphysically small. There is no theoretical justification for a more complex form for $l_{\min}$, and it fits the high-temperature upturn reasonably well. As explained below, little importance is attached to the quality of the fit above the plateau because it is just in this temperature range that the assumption of propagating phonons becomes invalid. Typical values for l at large ω are 4—10 Å, i.e., molecular dimensions.

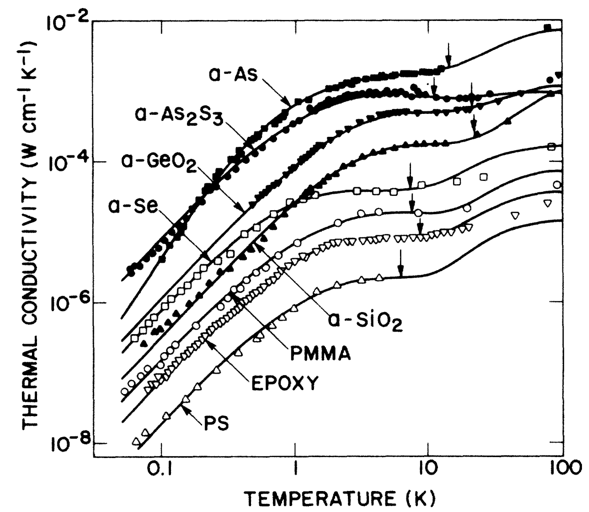

FIG. 2. Data of Fig. 1 displaced downward for clarity by successive factors of 2 from *a*-As (undisplaced). The symbols are the data points represented in Fig. 1 by smooth lines. The lines are numerical fits of Eq. (1) to the data. Each vertical arrow indicates the temperature T_L at which localization of the thermal phonons sets in (see the text).

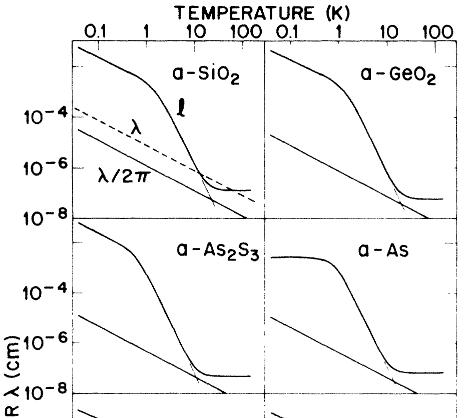

FIG. 3. Mean free path $l(\omega)$ for a temperature of 10 K, determined from the fits to the thermal-conductivity data in Fig. 2. Also shown is the inverse phonon wave vector $k^{-1}=\lambda/2\pi$ to indicate the point at which the localization condition $kl=1$ is met. The dashed line showing λ for *a*-SiO_2 is included to emphasize that $l(\omega)$ easily satisfies the somewhat less stringent condition $l=\lambda$. The temperature scale at the top indicates the temperature at which the average thermal phonon has angular frequency ω.

TABLE I. Parameters associated with the numerical fits shown in Figs. 2 and 3. Units are the following: ρ (g/cm^3), v (10^5 cm/sec), Θ_D (K), A (cm^{-1}K^{-1}), B (10^{-3} K^{-2}), D (cm^{-1}K^{-4}), $l_{\min}$ (Å), L (Å), T_L (K), $\tilde{n}\gamma^2$ (10^8 erg cm^{-3}), γ (eV), and G (10^{-4}).

Material	ρ	v	Θ_D	A	B	D	$l_{\min}$	L	T_L	$\tilde{n}\gamma^2$	γ	G
a-SiO$_2$	2.2	4.1	300	360	3.0	1.50	12	33	22	1.3	0.86	4.9
a-GeO$_2$	3.6	2.6	192	520	2.4	2.9	6	22	21	0.79	0.31	5.2
a-As$_2$S$_3$	3.2	1.69	93	330	0.6	2.9	5	27	11	0.13	0.04	5.0
a-As	4.77	1.56	160	110	2.0	16	7	20	14	0.049	0.09	5.0
a-Se	4.3	1.19	113	880	20	143	4	29	7	0.16	0.14	4.9
epoxy	1.22	1.66	140	1150	9	61	4	34	9	0.16	0.12	4.9
PMMA	1.2	1.79	150	1000	0.3	83	4	42	8	0.17	0.025	4.8
PS	1.0	1.67	123	2330	1.0	170	5	48	6	0.26	0.035	5.0

Least squares fits of Eq. (1) to the data of Fig. 1 using Eq. (2) for $l(\omega)$ are shown in Fig. 2. The frequency dependence of $l(\omega)$ for these fits is shown in Fig. 3, where we also plot the phonon wavelength $\lambda = 2\pi v/\omega$ and $k^{-1} = \lambda/2\pi$. The fitting parameters as well as density, velocity, and approximate Debye temperature are listed in Table I. The parameters are in reasonable agreement with previous fits to the thermal conductivity of a-SiO$_2$ (Refs. 2, 3, 5, and 11) and a-As (Ref. 4).

III. DISCUSSION

The values of $l(\omega)$ in Fig. 3 are, for the most part, larger than $\lambda(\omega)$, consistent with the assumption of propagating phonons. For $\omega < 10^{11}$ sec^{-1}, $l(\omega)$ varies as ω^{-1} due to resonant relaxation by TS's. An exception is a-As, which has few TS's but has a distribution of voids which effectively limits l to $l_{\max} \approx 29$ μm, where $l_{\max}^{-1}$ is added to l_t^{-1} and l_R^{-1} in Eq. (2).

For $\omega > 10^{11}$ sec^{-1}, the Rayleigh scattering term becomes important and l drops rapidly. Measured values[21] of $l(\omega)$ up to $\omega = 2\times 10^{12}$ sec^{-1} in a thin film of a-SiO$_2$ are in reasonably good agreement with this behavior. At higher frequencies, the intersection of $l(\omega)$ and $\lambda(\omega)$ indicates incipient localization and, indeed, the Ioffe-Regel criterion $kl = 1$ is met at somewhat higher frequency. We note that an extrapolation of the ω^{-4} mean free path intersects $\lambda/2\pi$ at a value which is very close to the l_m selected by the fitting routine. We take the intersection of this short extrapolation and $\lambda/2\pi(\omega)$ as an indication that the Ioffe-Regel condition is satisfied, and we do not expect Eq. (1) to be applicable at higher ω. The value of λ defined at this intersection and denoted L is listed in Table I for the glasses in Fig. 3. The frequency of the intersection is defined as ω_L. The temperature T_L for which the average phonon energy is $\hbar\omega_L$ ($T_L = \hbar\omega_L/2.7k_B$) is included in Table I and as vertical arrows on the data in Fig. 2. T_L occurs consistently near the upper end of the plateau, and the fits are markedly worse at higher temperatures. Poor agreement at high temperatures may be expected not only because of localization but also because the phonon spectrum is not known at these high temperatures, which are a large fraction of the Debye temperature. We note that, while the strength D of the Rayleigh scattering ranges over 2 orders of magnitude in Table I, the values of the localization length L span only a factor of 2. The latter indicates an intermediate range order with a remarkably invariant length scale of 20–50 Å for a wide range of glasses.

The results presented in Table I enable us to examine the variation of the fitting parameters from glass to glass. The TS scattering strength A yields values of $\tilde{n}\gamma^2$ which range over an order of magnitude. The values for a-SiO$_2$, a-As$_2$S$_3$, and a-Se agree reasonably with ultrasonic values:[27,29,30] 1.6×10^8, 1.4×10^7, and 5×10^6 erg cm^{-3}, respectively. Ultrasonic values of $\tilde{n}\gamma^2$ are not available for the other glasses. The coupling constant γ derived from B is only somewhat smaller than the measured[31] average value of 1.3 eV for a-SiO$_2$, the only case available. We conclude that the interaction of the propagating phonons with the tunneling systems is well described by the values of A and B in Table I.

We assume that the ω^4 scattering term represents Rayleigh scattering from local variations of the density or bond length,[2,4,8–11] which produce local variations in velocity. In the long-wavelength limit, a convenient expression[4] for the scattering strength caused by a mean-square velocity variation $G = \langle(\Delta v/v)^2\rangle$ is given by

$$D = 8k_B^4 G\xi^3/\hbar^4 v^4 , \tag{7}$$

where ξ is the correlation length of the fluctuations. Using $\xi = \lambda_L$ in Eq. (7), we obtain the values of G given in Table I. We find $G = 4.9 \pm 0.1\times 10^{-4}$, indicating a remarkably constant root-mean-square variation in velocity of 2.2% for all the glasses. While the values of G are reasonable,[4] we know of no theoretical argument that would account for such constancy in the amplitude of the velocity variations. We emphasize, however, the internal consistency of the present analysis. Ioffe-Regel localization indicates a correlation *length* L which, with the assumption of a (remarkably) constant *amplitude* of the velocity variations, accounts for the strength of the Rayleigh scattering. Previous calculations[4,11] have not been able to account for such strong Rayleigh scattering on the basis of density fluctuations. The important difference in the present case is our use of a longer correlation length L, rather than molecular dimensions.

The present study approaches the localization regime from the low-temperature, long-wavelength side. Recent work in aggregates[15] approaching from high temperatures and short wavelengths has revealed the upper end of a plateau occurring at a temperature at which λ equals the correlation length ξ. In this case ξ is approximately equal to the particle size. This was interpreted as phonon localization because the mean free path was also equal to the particle size. Those results, extrapolated to the plateau in bulk a-SiO$_2$, suggested $\xi \approx 30$ Å in a-SiO$_2$. That prediction agrees quite well with the wavelength (35 Å) for which $kl=1$ in Fig. 3.

The present analysis assumes linear dispersion of propagating phonons up to the frequency at which $kl=1$ ($\omega_L = 6\times10^{12}$ sec^{-1} for a-SiO$_2$). Measurements[22] to $\omega = 3\times10^{12}$ sec^{-1} show linear dispersion in an a-SiO$_2$ film. Extending the measurements up to ω_L should reveal any deviation from linearity that might occur as the Ioffe-Regel condition is met. In the absence of either measured or calculated dispersion in the vicinity of ω_L, we have assumed the simplest case, i.e., linear dispersion.

It has previously been noted[4,32–35] that there is a strong correlation between the temperature of the hump in C/T^3 and the temperature of the plateau in κ. The present results provide strong support for the suggestion[4,33–35] that the hump is due to the heat capacity of localized modes.

The generality of the present analysis does not allow us to distinguish among various models for the localized modes. In particular, we cannot infer that the modes are fractons,[13,14] since there is no evidence that the structure of a bulk glass is fractal.

Thermal-conductivity data[38] for a series of Araldite epoxy samples have been cited[39] as qualitative evidence for a fracton density of states. The data, Fig. 4, include results for different amounts of hardener, ranging from 37% to 4 times the stoichiometric amount. (The sample with the smallest concentration of hardener seems to be qualitatively different from the others and we exclude it from the present discussion.) The effect of adding more hardener is to increase the conductivity, especially at temperatures near the lower end of the plateau, and to cause an apparent shift in the plateau toward higher temperatures. This apparent shift toward shorter thermal wavelengths is claimed[39] to support a fracton model because it is supposed that the increased amount of cross linking that occurs with increased hardener concentration shortens the characteristic molecular length scale, which is thought to determine a phonon-fracton crossover frequency.

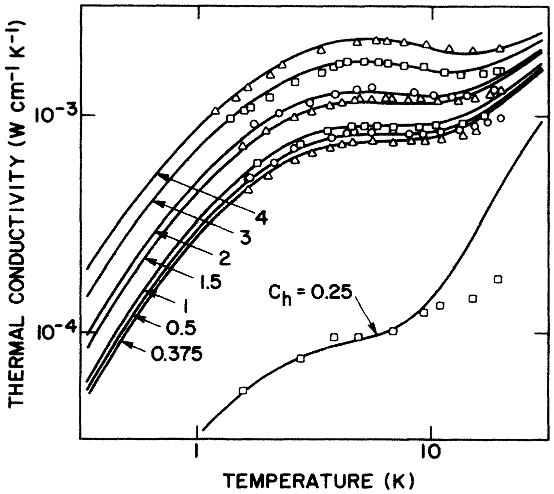

FIG. 4. Thermal conductivity of a series of Araldite epoxy samples with different amounts of hardener (Ref. 38). C_h is the hardener concentration relative to the stoichiometric hardener concentration. The lines through the data represent computer fits described in the text.

These arguments can be tested quantitatively by using the same analysis and fitting scheme described above for bulk glasses. The results are shown in Fig. 4 as calculated curves for the thermal conductivity which reproduce the data quite reasonably. As suggested by Farrell *et al.*,[38] the same mean velocity is used for all the samples. The Debye cutoff frequency Θ_D is taken arbitrarily as 140 K for all samples, for lack of more information. The choice of Θ_D affects the high-temperature conductivity but, as described above, it is just in the high-temperature regime that localization takes place and the propagating-mode analysis breaks down. Thus, little importance can be attached to the value of Θ_D or the quality of the fit above 10–15 K. The three parameters determining the fit for the remaining temperature range are the scattering strengths A and B and the Rayleigh scattering strength D, shown in Fig. 5. The analysis indicates a strong decrease in TS scattering strength with hardener concentration, most easily interpreted as a decrease in the number of TS per unit volume. This is in agreement with the original (nonfractal) interpretation of the data.[38] In contrast, the Rayleigh scattering strength is nearly indepen-

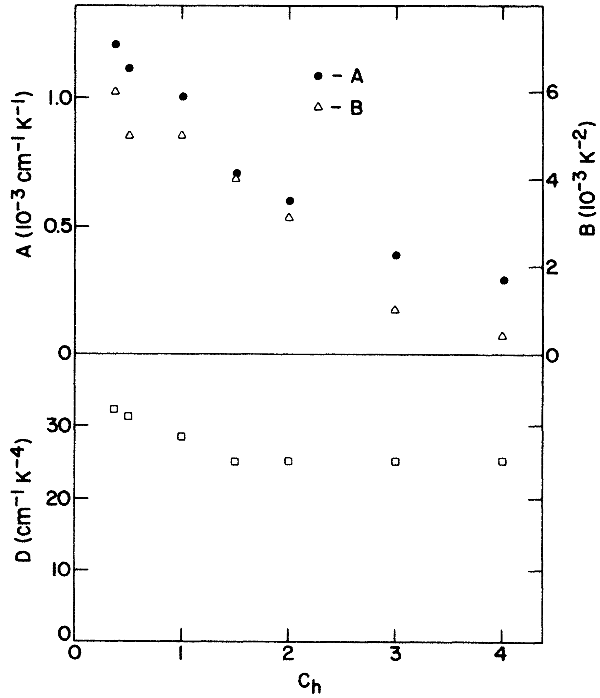

FIG. 5. Parameters A and B (resonant and relaxational TS scattering strengths) and D (Rayleigh scattering strength) for the epoxy data in Fig. 4 as a function of the relative hardener concentration C_h.

dent of hardener concentration, indicating that the apparent shift in the temperature of the plateau is due primarily to a change in the number of TS. The constancy of D indicates a constant value of L, which turns out to be 26 Å for all the epoxy samples in Fig. 4. This value is similar to those of other bulk glasses in Table I. Thus any change that may occur in cross linking does not have a strong effect on the characteristic length scale revealed by Rayleigh scattering of thermal phonons.

The data of Fig. 4 therefore do not support the suggestion[13] that bulk glasses are fractal. In our opinion, the dynamics of bulk glasses are better described in terms of phonon localization due to strong scattering from static density fluctuations. A fracton model is more appropriately tested using materials with a demonstrably fractal structure, such as aggregates of small particles.[15,40]

IV. CONCLUSION

Examination of the thermal conductivity of a wide variety of glasses at low temperatures reveals that the Ioffe-Regel criterion for phonon localization is satisfied in the region of the plateau. This is compared to earlier work in aggregates where localization occurs on a length scale determined by the correlation length of the structure. Together, these results indicate a correlation length of ~ 30 Å in bulk a-SiO$_2$, for example. Glass-to-glass variations in the wavelength at which localization occurs are minor, spanning the range 20—50 Å. The use of this Ioffe-Regel localization length allows for a better quantitative understanding of Rayleigh scattering in glasses than is possible using a correlation length of molecular dimensions.

Examination of the thermal conductivity of a series of epoxy samples with varying hardener-to-resin ratio reveals a similar correlation length for all samples. The data can be explained by a varying amount of scattering from tunneling systems, without the need for a phonon-fracton crossover as previously suggested.

More generally, we have established a strong correlation between the plateau in disordered structures and the localization of phonons associated with heavy scattering, and we have shown that this localization occurs for phonon wavelengths comparable to a correlation length of the disordered structure.

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[1] *Amorphous Solids: Low Temperature Properties,* edited by W. A. Phillips (Springer-Verlag, Berlin, 1981).

[2] M. P. Zaitlin and A. C. Anderson, Phys. Rev. B **12**, 4475 (1975).

[3] T. L. Smith, P. J. Anthony, and A. C. Anderson, Phys. Rev. B **17**, 4997 (1978).

[4] D. P. Jones, N. Thomas, and W. A. Phillips, Philos. Mag. B **38**, 271 (1978).

[5] D. P. Jones and W. A. Phillips, Phys. Rev. B **27**, 3891 (1983).

[6] R. Maynard, in *Phonon Scattering in Solids,* edited by L. J. Challis, V. W. Rampton, and A. F. G. Wyatt (Plenum, New York, 1976), p. 115.

[7] A. J. Leadbetter, A. P. Jeapes, C. G. Waterfield, and R. Maynard, J. Phys. (Paris) **38**, 95 (1977).

[8] R. C. Zeller and R. O. Pohl, Phys. Rev. B **4**, 2029 (1971).

[9] G. J. Morgan and D. Smith, J. Phys. C **7**, 649 (1974).

[10] D. Walton, Solid State Commun. **14**, 335 (1974); Phys. Rev. B **16**, 3723 (1977).

[11] J. Jäckle, in *The Physics of Non-Crystalline Solids,* edited by G. H. Frischat (Transtech, Aedermannsdorf, 1977), p. 568.

[12] D. P. Jones, J. Jäckle, and W. A. Phillips, in *Phonon Scattering in Condensed Matter,* edited by H. J. Maris (Plenum, New York, 1980), p. 49.

[13] S. Alexander, C. Laermans, R. Orbach, and H. M. Rosenberg, Phys. Rev. B **28**, 4615 (1983).

[14] P. F. Tua, S. J. Putterman, and R. Orbach, Phys. Lett. **98A**, 357 (1983).

[15] J. E. Graebner, B. Golding, L. C. Allen, and W. H. Haemmerle, Bull. Am. Phys. Soc. **30**, 315 (1985); J. E. Graebner and B. Golding, Phys. Rev. B **34**, 5788 (1986).

[16] A. F. Ioffe and A. R. Regel, Prog. Semicond. **4**, 237 (1960).

[17] S. John, H. Sompolinsky, and M. J. Stephen, Phys. Rev. B **27**, 5592 (1984).

[18] E. Akkermans and R. Maynard, J. Phys. (Paris) Lett. **46**, L-1045 (1985); E. Akkermans and R. Maynard, Phys. Rev. B **32**, 7850 (1985).

[19] P. W. Anderson, Phys. Rev. **109**, 1492 (1958).

[20] E. Abrahams, P. W. Anderson, D. C. Licciardello, and T. V. Ramakrishnan, Phys. Rev. Lett. **42**, 673 (1979).

[21] W. Dietsche and H. Kinder, Phys. Rev. Lett. **43**, 1413 (1979).

[22] M. Rothenfusser, W. Dietsche, and H. Kinder, in *Phonon Scattering in Condensed Matter,* edited by W. Eisenmenger, K. Lassmann, and S. Döttinger (Springer-Verlag, Berlin, 1984), p. 419.

[23] R. B. Stephens, Phys. Rev. B **8**, 2896 (1973); **13**, 852 (1976).

[24] S. Kelham and H. M. Rosenberg, J. Phys. C **14**, 1737 (1981).

[25] W. H. Haemmerle and B. Golding, Bull. Am. Phys. Soc. **24**, 282 (1979).

[26] S. Hunklinger and L. Piché, Solid State Commun. **17**, 1189 (1975).

[27] B. Golding, J. E. Graebner, and R. J. Schutz, Phys. Rev. B **14**, 1660 (1976).

[28] J. E. Graebner and L. C. Allen, Phys. Rev. B **29**, 5626 (1984).

[29] C. Laermans, L. Piché, W. Arnold, and S. Hunklinger, in *The Physics of Non-Crystalline Solids,* Ref. 11, p. 562.

[30] G. Bellessa, C. Lemercier, and D. Caldemaison, Phys. Lett. **62A**, 127 (1977).

[31] B. Golding and J. E. Graebner, Phys. Rev. Lett. **37**, 852 (1976); J. E. Graebner and B. Golding, Phys. Rev. B **19**, 964 (1979).

[32] A. J. Leadbetter, in *Proceedings of the International Conference on Phonon Scattering in Solids,* edited by H. Albany (Centre d'Etudes Nucléaires de Saclay, Gif-sur-Yvette, France, 1972), p. 338.

[33] W. A. Phillips, J. Non-Cryst. Solids **31**, 267 (1978).

[34] D. A. Ackerman, D. Moy, R. C. Potter, A. C. Anderson, and W. N. Lawless, Phys. Rev. B **23**, 3886 (1981).

[35] W. M. MacDonald, A. C. Anderson, and J. Schroeder, Phys. Rev. B **32**, 1208 (1985).

[36] K. Guckelsberger and J. C. Lasjuanias, Compt. Rend. **270**, B1427 (1970).

[37] R. B. Stephens, G. S. Cieloszyk, and G. L. Salinger, Phys. Lett. **38A**, 215 (1972).

[38] D. E. Farrell, J. E. de Oliviera, and H. M. Rosenberg, in *Phonon Scattering in Condensed Matter,* edited by W. Eisenmenger (Springer-Verlag, 1983), p. 422.

[39] R. Orbach and H. M. Rosenberg, *Proceedings of LT-17,* edited by U. Eckern, A. Schmid, W. Weber, and H. Wuhl (Elsevier, New York, 1984), p. 375.

[40] J. H. Page and R. D. McCulloch, Phys. Rev. Lett. **57**, 1324 (1986).