lower frequencies when $\omega\tau_\perp \ll 1$, sound travels at the adiabatic velocity corrected by the coupling to second sound.[18] In the frequency and temperature range investigated by Abraham et al.,[7,9] $\omega\tau_\perp \gg 1$. A possible interpretation of these velocity measurements is that the decrease in velocity observed as the frequency increases arises from a transition from parallel sound to zero sound. This would require $\Delta c_\parallel > \Delta c_0$. This is possible because $\Delta c_\parallel$ may be large and positive if γ and δ are such that the average group velocity $\langle v_p \rangle$ of the thermal phonons is nearly equal to the velocity c of the sound wave.

A more detailed discussion of these points must await measurements of the helium dispersion curve to lower momenta and more exact solutions of the transport equations. We note that even the recent measurements of Woods and Cowley still do not reach that part of the spectrum that is thermally excited in the temperature range discussed in this paper.

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[18] See Wilks, Ref. 16, Chap. 8.

RAMAN-SCATTERING SELECTION-RULE BREAKING AND THE DENSITY OF STATES IN AMORPHOUS MATERIALS*

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We present a calculation of the dielectric correlation function in glasses showing how the assumption of short correlation length for normal modes breaks the momentum selection rules and leads to expressions for the first-order Raman-scattering intensity in terms of the density-of-states functions and known frequency-dependent amplitudes.

Because of the current interest in Raman scattering and the properties of amorphous solids, we have been attempting to understand the shapes of the bands observed in Raman scattering of glasses. In the most frequently studied substance, vitreous silica, good data are available at room temperature[1] and low temperatures[2,3] but an adequate interpretation of the scattering in glasses giving the observed bands has been lacking.

In this Letter we present the outline of a calculation leading to an equation for the spectral scattering intensity in terms of the density of states of the vibrations in amorphous materials. The results are applied to Raman-scattering data of vitreous silica.

Minimal assumptions about the vibrational modes of a glass are made: (1) The vibrations are harmonic so that they can be analyzed into normal modes; (2) the vibrations couple to light through the displacement dependence of the electronic polarizability of the material; and (3) the coherence length of the normal modes is short compared with optical wavelengths. The assumption of short coherence lengths yields the breakdown of the usual wave-vector selection rules and allows the light-scattering process to occur from essentially all the normal modes of the material. This is the only assumption that is different for amorphous materials compared with crystals.

The spectral scattering cross section is proportional to the space-time Fourier components of the scattering perturbation space-time autocorrelation function.[4] For light scattering we need to treat the variations in the local optical dielectric tensor $\epsilon_{\alpha\beta}(\vec{r}, t)$ of the medium.

Scattering cross sections for all possible experiments are proportional to linear combinations of the space-time Fourier components of the correlation functions of the dielectric fluctuations

$$G_{\alpha\beta,\gamma\delta}(\vec{r}, t) = \langle \Delta\epsilon_{\alpha\beta}(\vec{r}\,', t')\Delta\epsilon_{\gamma\delta}(\vec{r}\,'+\vec{r}, t'+t)\rangle. \tag{1}$$

We consider the modulation of the optical dielectric constant by normal-mode vibrations by expanding the dielectric tensor to first order in atomic displacements, and express the displacements in terms of normal coordinates $Q_j(t)$ for the jth mode. We have the deceptively simple form

$$\Delta\epsilon_{\alpha\beta}(\vec{r}, t) = \sum_{j=1}^{3N} \frac{\partial\epsilon_{\alpha\beta}(\vec{r})}{\partial Q_j} Q_j(t). \tag{2}$$

The derivatives $\partial\epsilon/\partial Q$ are in general nonzero unless a local symmetry such as inversion symmetry causes cancellations of the contributions from neighboring atom displacements.

When the expansion in normal modes (2) is substituted in the correlation functions (1) one finds

$$G_{\alpha\beta,\gamma\delta}(\vec{r}, t) = \textstyle\sum_j R_{\alpha\beta,\gamma\delta}(\vec{r}, j)\langle Q_j(t')Q_j(t'+t)\rangle, \tag{3}$$

where

$$R_{\alpha\beta,\gamma\delta}(\vec{r}, j) = \left\langle \frac{\partial\epsilon_{\alpha\beta}(\vec{r}\,')}{\partial Q_j} \frac{\partial\epsilon_{\gamma\delta}(\vec{r}\,'+\vec{r})}{\partial Q_j} \right\rangle. \tag{4}$$

This important result shows how the space and time correlations separate for each mode j. To derive it we have made use of the statistical independence of the normal coordinates of different modes. Using the properties of harmonic oscillators it is easy to show that[5]

$$\langle Q_j(t')Q_j(t'+t)\rangle = \frac{\hbar}{2\omega_j}\{n(\omega_j)e^{i\omega_j t} + [1+n(\omega_j)]e^{-i\omega_j t}\}, \tag{5}$$

where $n(\omega_j) = [\exp(\hbar\omega_j/kT)-1]^{-1}$. Thus the time correlations are known, and we need only to discuss the possible space correlations to apply our result to scattering.

The expression (3) with (4) and (5) is quite general. It applies to any vibrational Raman scattering from solids whether crystalline or amorphous. The distinction between crystals and amorphous materials lies in the size of the region over which the correlation function extends. The spatial correlation functions of the dielectric fluctuations $R(\vec{r}, j)$ essentially reflect just the spatial correlations of the atomic displacements of the normal modes. Hence the correlation range of $R(\vec{r}, j)$ will be that of the mode j. In an ideal crystal, lattice dynamics shows us that because of the periodicity of the lattice, the normal-mode vibrations are wavelike with infinite extent. Correspondingly the spatial correlation functions $R(\vec{r}, j)$ would have a sinusoidal dependence on r with wavelength $\lambda_j = 2\pi/q_j$. The light-scattering spectrum then can only show frequencies ω_j for which the mode j has a wave vector $\vec{q}_j$ equal to the scattering vector $\vec{q}$. This is the usual "momentum" selection rule for crystals which gives rise to the discrete set of lines seen in crystal spectra.

In a real crystalline sample the mode correlation functions are of finite extent due to various defect and coupled phonon damping mechanisms but they still extend over distances large compared with the wavelength of light. Thus the crystal momentum selection rule remains a useful approximation.

In amorphous materials translational symmetry which characterized crystals is lost causing the correlation functions to be localized. We assume for the present discussion that the modes have coherence lengths of $\frac{1}{10}$ optical wavelengths (400 Å) or less. Such modes will not be characterized by a single wave vector and will not give a momentum selection rule.

This assumption of a short range for $R(\vec{r}, j)$ has the immediate consequence that its Fourier transform has a broad flat maximum around $\vec{q}=0$ instead of being sharply peaked at a particular wave vector $\vec{q}_j$. This will be true for all j, so all the modes of the material can give contributions to the light-scattering spectrum. The spatial Fourier transform of the correlation functions with range Λ_j in the limit $q\Lambda_j \ll 1$ has the limiting form

$$\{R_{\alpha\beta,\gamma\delta}(\vec{r}, j)\}_{\vec{q}} = A_{\alpha\beta,\gamma\delta}(j)\Lambda_j^{3} \tag{6}$$

independent of $\vec{q}$. $A(j)$ measures the strength of the dielectric modulation of the mode and Λ_j^3 is essentially the volume of the region of coherence of the mode.

With this approximation the space-time components of the dielectric correlations for light-scattering wave vectors become

$$G_{\alpha\beta,\gamma\delta}(\vec{q}, \omega) = \sum_{j=1}^{3N} A_{\alpha\beta,\gamma\delta}(j)\Lambda_j^{3}(\hbar/2\omega_j)\{n(\omega_j)\delta(\omega+\omega_j)+[1+n(\omega_j)]\delta(\omega-\omega_j)\}. \tag{7}$$

The delta functions $\delta(\omega+\omega_j)$ give the anti-Stokes components (upshifted scattered light) and the delta functions $\delta(\omega-\omega_j)$ give the Stokes components (downshifted scattered light). This expression shows that all modes will contribute to the Raman spectrum of amorphous materials but with an unknown weighting factor composed of the optical coupling tensor $A_{\alpha\beta,\gamma\delta}(j)$ and the mode volume Λ_j^3.

We expect the normal vibrations to fall into bands having similar microscopic motions, frequencies, optical coupling, and correlation ranges, e.g., stretching bands, bending bands, etc. Thus we will use the approximation of replacing the terms $A(j)(\Lambda_j)^3$ by a constant for all the modes of a given band, in particular assuming this constant to be independent of the frequencies of the modes in the band. The sum over all modes then breaks into a set of sums over modes in bands. The frequencies are closely spaced. Thus the discrete sums can be replaced by the density-of-states functions for each band, where the density of states gives the number of modes per unit frequency. With these assumptions the Stokes spectrum shape will be

$$I_{\alpha\beta,\gamma\delta}(\omega) = \sum_b C_b^{\alpha\beta,\gamma\delta}(1/\omega)[1+n(\omega)]g_b(\omega). \tag{8}$$

The sum is over all the bands. The constants $C_b^{\alpha\beta,\gamma\delta}$ will depend on the band b. The tensor components labeled $\alpha\beta, \gamma\delta$ are selected by the polarization of the incident and scattered light. $g_b(\omega)$ is the band density of states.

The frequency-dependent factors $1/\omega$ and $1+n(\omega)$ of Eq. (8) change the shape of the contribution from that of a band with density of states $g_b(\omega)$. This is particularly striking for the low-frequency bands seen in all glasses which extend to $\omega=0$ where these vibrational maplitude factors cause a peak to appear in the Raman spectrum.[2,3] Note that the factor $1+n(\omega)$ is just the thermal population of the initial states and occurs in all expressions for the Raman intensity. The additional frequency-dependent factor $1/\omega$ is also rigorously correct for vibrations but is usually suppressed in discussing intensities. Here where we are interested in band shapes over large frequency ranges it is important to take it into account.

The expression for the spectral shape (8) is the principal result of our calculation. It shows how the vibrational density of states of amorphous materials contributes to the shape of the scattering spectrum. We see that, even with our extreme assumptions of assigning frequency-independent coupling constants and correlation ranges to whole bands, the spectrum can be very complicated due to overlapping bands and differing coupling constants.

As an example of the use of (8) in the interpretation of Raman spectra, we show in Fig. 1 experimental Raman polarized spectrum intensities[7] for vitreous silica reduced by the thermal population factor $[1+n(\omega)]$ and the full frequency-dependent vibrational intensity factor $[1+n(\omega)]/\omega$ plotted together with the density-of-states histogram for vitreous silica calculated by Bell, Bird, and Dean.[6] We see that the factor $1+n(\omega)$ alone gives apparent agreement with Dean's histogram,

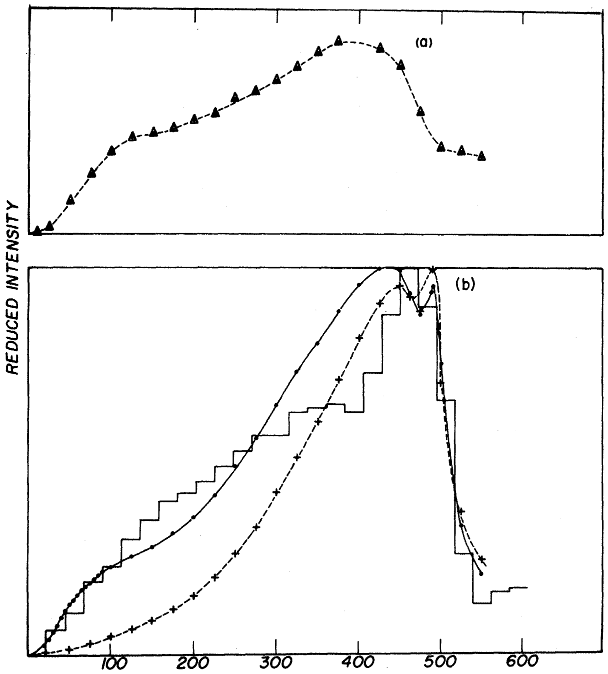

FIG. 1. Fused silica. (a) VH polarized spectrum reduced by $[1+n(\omega)]/\omega$ (b) Dashed line, VV polarized spectrum reduced as in (a); line with dots, VV polarized spectrum reduced by $[1+n(\omega)]$. The histogram is the density of states from the calculations of Bell, Bird, and Dean (Ref. 6).

but this is misleading. In fact, a large number of modes contribute at low frequencies but are most easily detected in the VH spectrum.

The fully reduced VV spectral data by themselves do not agree well with Dean's calculation. We think this is due to the different coupling constants C_b.

The low-frequency part of the spectrum contains the modes dominating the thermodynamic properties. We have used our data to obtain a shape for the low-frequency density of states which gives a calculated heat capacity temperature dependence in agreement[8] with the measured anomaly.[1]

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FREQUENCY DEPENDENCE OF THE CYCLOTRON MASS AND OF THE RELAXATION TIME IN LEAD AND MERCURY

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We report a series of Azbel'-Kaner cyclotron resonance experiments in lead and mercury at wavelengths varying from 9 to 1 mm. We observe that in both metals the electron-phonon relaxation time is frequency dependent ($\tau \propto \omega^{-2}$ in lead), and that the effective mass increases slightly for the highest frequency in mercury ($3 \mp 1\,\%$ at $\lambda = 1$ mm).

The electron-phonon interaction theory predicts a change of the electron effective mass and relaxation time when the electron is excited far from the Fermi energy. In a cyclotron resonance experiment this excitation above the Fermi level can be obtained either by an increase of frequency[1] or by an increase of temperature.[2,3] The temperature effect has already been observed in zinc[4] and lead.[5] The present work is the first experimental evidence of the frequency dependence of the effective mass m^* and of the relaxation time τ in metals.

The theoretical predictions of Scher and Holstein[1] are the following: When the microwave frequency becomes of the same order of magnitude as the Debye frequency, the effective mass of the electron should increase slightly and the relaxation time should decrease as ω^{-3}. We