Structure in the Brillouin Spectra of Thin Films

J. R. Sandercock
Laboratories RCA Ltd., Zurich, Switzerland
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Unsupported films with thicknesses of the order of the wavelength of light are shown to have Brillouin peaks with triplet or quadruplet structure, reflecting the discrete values of the phonon wave vector perpendicular to the surface of the film. The observation of this structure in the spectra of a polymer and a crystal film is reported here. The feasibility of making a high-frequency phonon spectrometer using thin films is discussed.

Recently, I reported the results of some Brillouin backscattering measurements on opaque materials.[1] The Brillouin peaks were found to be Lorentzian broadened as a result of the strong light absorption which effectively limited the scattering volume to within a few wavelengths of light from the surface. The natural sequel to these measurements, with interesting possibilities in the field of phonon spectrometry, is the observation of Brillouin scattering from thin films. In this case the sharp boundaries to the scattering volume imposed by the film surfaces lead to a broadening in the Brillouin peaks of the form $(\sin^2 x)/x^2$ when the film thickness d is of the order of the wavelength of light. If, further, the film is unsupported, the boundary conditions require that the component of the phonon wave vector perpendicular to the surface be an integral multiple of π/d. This requirement modulates the $(\sin^2 x)/x^2$ envelope and gives a triplet or quadruplet Brillouin peak with further structure in the wings of the envelope.

The form of the spectrum may be calculated straightforwardly for the case of 180° backscattering perpendicular to the surface. Following Ref. 1 and taking z as the normal to the surface, we may show that, in general, the backscattered field E_S at frequency ω is given by

$$E_S \sim \exp(i\omega t) \int dq_z \int dz \exp[i(2nk_0 - q_z)z],$$

with $\omega = \omega_0 \pm \Omega(\vec{q})$, where ω_0, k_0 refer to the incident light, $\Omega(\vec{q})$, $\vec{q}$ to the phonon, and n is the refractive index. The integral over the dimensions of the scattering volume parallel to the surface has already been carried through and leads to the requirement that $\vec{q}$ be parallel to z, since it is assumed that the dimensions parallel to the surface are large compared to the wavelength of light.

The integral over z has three distinct regimes.

(a) Where n is real and z extends to ∞, the integral is the δ function $\delta(2nk_0 - q_z)$ which leads to the normal Brillouin shift $\Omega_0 = 2nk_0 v$ (v is the sound velocity) as illustrated in Fig. 1(a), where some instrumental and phonon lifetime broadening of the peaks has been assumed.

(b) Where n is complex and z extends to ∞, the integral leads to a Lorentzian broadening in the scattered power as discussed in Ref. 1.

(c) Where n is real and z bounded $(0 < z < d)$, the integral describes the scattering from a transparent film and gives

$$E_S \sim \int dq_z \frac{\exp[i(2nk_0 - q_z)d] - 1}{i(2nk_0 - q_z)}.$$

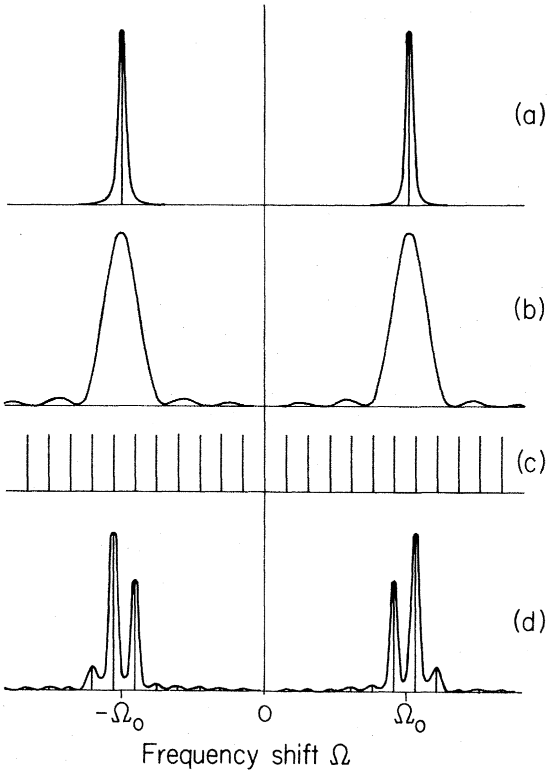

FIG. 1. (a) A normal Brillouin spectrum, (b) the expected spectrum from a thin supported film, (c) the possible frequency shifts in the spectrum from a thin unsupported film, and (d) the observable spectrum from a thin unsupported film.

The power P_S scattered per unit solid angle around the direction z is proportional to $|E_S|^2$, whence

$$P_S \sim \int dq_z \frac{\sin^2[(2nk_0 - q_z)d/2]}{[(2nk_0 - q_z)d/2]^2}. \tag{1}$$

If the film is assumed to be mounted on a substrate with the same acoustic impedance (though elasto-optically different, so that we may assume that Brillouin scattering occurs only from the film), then the phonons occupy virtually a continuum in q space, and we may write the power $(dP_S/d\Omega)(\omega_0 \pm \Omega)d\Omega$ in the frequency range $d\Omega$ as

$$\frac{dP_S}{d\Omega}(\omega_0 \pm \Omega)\, d\Omega \sim \frac{d\Omega \sin^2[(\Omega_0 - \Omega)d/2v]}{[(\Omega_0 - \Omega)d/2v]^2}. \tag{2}$$

This spectrum is shown in Fig. 1(b). The Brillouin peaks are centered around the normal Brillouin frequencies $\omega_0 \pm \Omega_0$. The width of the peaks $\Delta\Omega$, defined as the full width at the points halfway to the first minima, is seen to be given by $\Delta\Omega/\Omega_0 = \lambda_0/2nd$, where $\lambda_0 = 2\pi/k_0$ is the wavelength of the incident light.

The situation is rather different for the case of an unsupported film, where, as mentioned above, the boundary conditions require that $q_z = p\pi/d$, where p is an integer. Equation (1) may then be written as

$$P_S \sim \sum_p \frac{\sin^2(\Omega_0 d/2v - p\pi/2)}{(\Omega_0 d/2v - p\pi/2)^2}. \tag{3}$$

The spectrum thus has peaks at the frequency shifts $\Omega = q_z v = p\pi v/d$ with relative amplitudes determined by the $(\sin^2 x)/x^2$ envelope. The possible frequency shifts $\Omega = p\pi v/d$ are shown in Fig. 1(c). The amplitudes, as determined by Eq. (3), are shown in Fig. 1(d), where again some instrumental and lifetime breadening has been assumed. It will be observed that the interval between the possible frequency shifts is just half the interval between the maximum and the first minimum of the $(\sin^2 x)/x^2$ envelope, reflecting the fact that for normal 180° backscattering the phonon wave vector is twice the incident photon wave vector. The exact form of the peaks of Fig. 1(d) depends on the thickness d, but in general they will show triplet or quadruplet structure within the main peak of the $\sin^2 x/x^2$ envelope, with weaker structure in the wings of the envelope. For the particular case that Ω_0 corresponds to one of the possible frequency shifts, the Brillouin peaks are symmetrical triplets with a single weak peak in each wing of the envelope.

The results of some measurements on thin films are reported here. The measurements were made in a near-backscattering arrangement using a single-frequency argon laser operating at 5145 Å. The spectra were resolved using a multipassed interferometer described elsewhere.[2,3]

The first material investigated was a film of collodion obtained by dipping a loop of wire into a solution of collodion in ether. As a result of the rather short phonon lifetime in this material, it was found necessary to measure a film with a thickness of less than 1 μm in order to resolve the structure. Figure 2(a) shows a typical spectrum, this one corresponding to the symmetrical triplet discussed above. The optical thickness of the film at the measurement point was obtained by an interference method and this value used to predict the peak positions using Eq. (3). The vertical lines are the predicted positions and are in good agreement with the observed positions. The background scattering was strong enough to mask any further structure in the spectrum. There is a suggestion of a peak at about 0.23 cm^{-1} whose origin is obscure. It may arise from scattering from a damped transverse phonon mode, but such an explanation is doubtful since previous Brillouin measurements on polymers have never revealed such a peak.[4]

The second material investigated was the layer compound Mn_2PS_4 which had been prepared some years ago in this laboratory by Nitsche.[5] A trial measurement on a thick crystal showed this material to have a strong Brillouin spectrum with narrow peaks. As a result it proved possible to observe structure in the Brillouin peaks from specimens up to about 5 μm in thickness. Figure 2(b) shows a nearly symmetrical triplet, well resolved, but with none of the weak structure apparent. The peaks are observed in the first adjacent order. The wing on the Rayleigh line results from forward scattering from the light reflected off the second surface of the crystal and is seen in the zeroth order. Figure 2(c) shows the triplet spectrum from a thicker specimen in which, in addition, the weaker peaks arising from the first subsidiary maxima in the $(\sin^2 x)/x^2$ envelope are just resolved.

The important conclusion to be drawn from these measurements and from the foregoing discussion is that by physically restricting the depth of the scattering volume, the requirement of momentum conservation in this direction in the scattering process is relaxed to a degree inversely proportional to the depth of the scattering volume. Thus, while normal Brillouin scattering (i.e.,

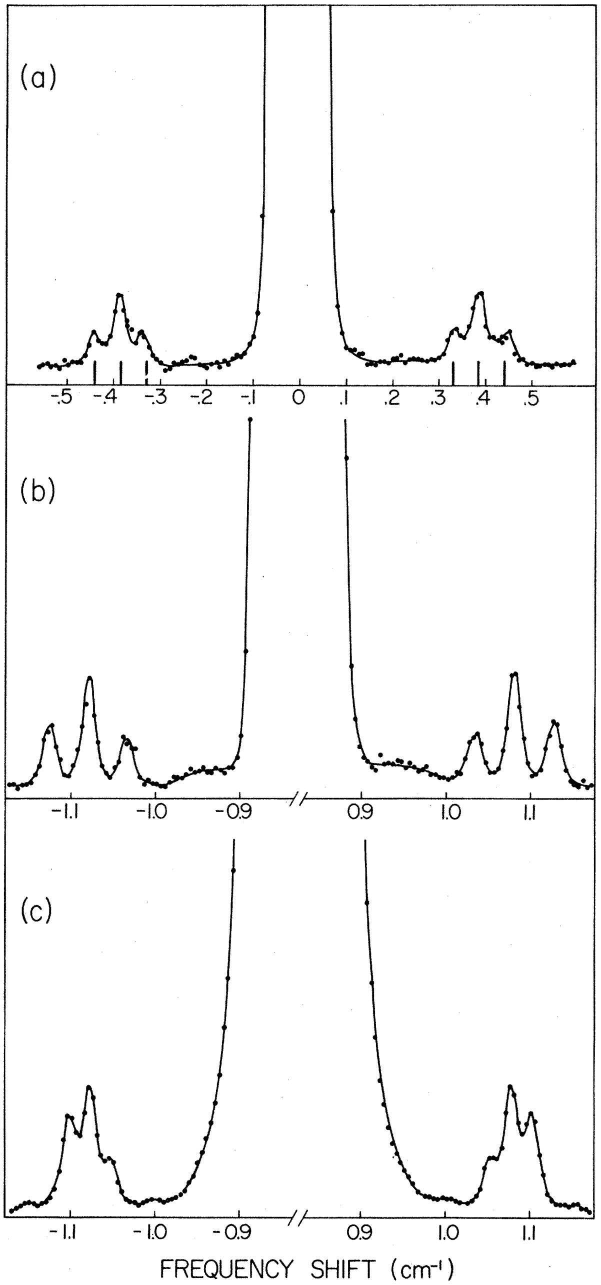

FIG. 2. Observed spectra from (a) a collodion film and (b), (c) two specimens of Mn_2PS_4 of thickness 1.1 and 2.0 μm, respectively.

from a large volume) determines precisely both the energy (from the spectrum) and the momentum (from the scattering geometry) of the phonon involved, the scattering from a thin film determines the phonon energy precisely but the momentum only imprecisely. A light scattering measurement on a thin film thus measures phonons within a range of momenta and correspondingly having a range of energies. The bandwidth $\Delta\Omega$ for the phonon detection was shown by Eq. (2) to be given by $\Delta\Omega/\Omega_0 = \lambda_0/2nd$, where $\Omega_0 = 2nk_0v$ is the phonon frequency determined in a normal backscattering measurement. Figure 1(b) which represents Eq. (2) may be interpreted as the phonon detection sensitivity as a function of phonon frequency. By choosing the film thickness d such that $\Delta\Omega > \Omega_0$ (i.e., $d \leq 1000$ Å) Eq. (2) shows that the detection sensitivity is finite for all phonons traveling perpendicular to the film with frequencies in the range $0 < \Omega < \Omega_0 + \Delta\Omega$. While Ω_0 is the maximum acoustic phonon frequency normally detectable in a light scattering experiment and is typically less than 100 GHz, the corresponding measurement on a thin film detects up to a maximum frequency of $\Omega_0 + \Delta\Omega$. The film could thus supply the basis of a high-resolution high-frequency phonon spectrometer in which the film would be mounted on the material under investigation. Phonons generated by external means and propagating through the material would be detected by a light-scattering measurement on the film, allowing the phonon frequency spectrum, and by suitable gating, the time of flight as a function of frequency to be determined.

In practice, it may be difficult to perform such measurements. Firstly, the film must be acoustically matched to the substrate in order that the phonons can get into the film, and secondly a means must be found to prevent the light entering the substrate, since the scattered light must come only from the film. Furthermore, the greater the desired bandwidth, the smaller the film thickness must be and, consequently, the weaker the spectrum of the scattered light will be. It is felt, however, that these difficulties are not insurmountable and some experiments to test the practicability of such a spectrometer will be made in the near future.

At the present time, apart from inelastic-neutron-scattering spectrometers, there are very few phonon spectrometers working in this frequency range of up to a few hundred gigahertz. Systems such as the superconducting tunnel-junction system described by Kinder,[6] which rely on the generation of monochromatic phonons, do not have the same potential applications as a spectrometer capable of analyzing the frequency spectrum of a phonon source. Of such spectrometers there appear to be only two, namely, the paramagnetic spin spectrometer of Anderson and Sabisky[7] and the "hole-burning" Sb-doped Ge spectrometer described by Dynes, Narayanamurti, and Chin.[8] Both these devices, however, offer elegant solutions only to a limited range of low-temperature experiments. On the other hand, a thin-film light-scattering spectrometer could, in principle, be applied to any solid and would not be restricted to low-temperature operation. Within its frequency range such a device could thus be a versatile complement to the inelastic-neutron-scattering spectrometers.

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Hopping Conduction through Localized States in Nb/Al_2O_3 Films*

A. Devenyi†
Physikalisches Institut der Universität Karlsruhe, Karlsruhe, West Germany

and

R. Manaila-Devenyi
Institute of Physics, Bucharest, Romania

and

R. M. Hill
Chelsea College, University of London, Pulton Place, London SW7, England

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Electrical conduction in Nb/Al_2O_3 cermet films at low temperatures shows the presence of a new form of hopping conduction through localized states. In this mechanism the dielectric plays an essential role, behaving like an amorphous wide-band-gap semiconductor and acting as host to a distribution of localized states due to Nb dispersed, on an atomic scale, in the alumina matrix.

Electrical transport phenomena in thin films, obtained by co-deposition of a metal and a dielectric, have been extensively investigated of late because of their applications as resistive elements. These materials are also interesting from the point of view of electrical transport in disordered systems.[1-5]

Thin films of Nb/Al_2O_3 were obtained by coevaporation from two independent sources onto fused-silica substrates. A detailed account of the preparation, structural investigation, and superconductivity of these films will be published elsewhere.[6]

Electron-microscope investigation showed the films to consist of quasispherical niobium particles imbedded in an Al_2O_3 matrix. In order to obtain different particle sizes, we varied the concentration of Nb as well as the temperature of deposition and annealing.

Films containing 85–95 wt% Nb, as known from the controlled evaporation parameters, were deposited on substrates maintained at 550°C and had a mean particle size $2r$ of about 32 Å. These films showed metallic-type conduction with a relatively small temperature coefficient of resistivity ($+6.6\times10^{-4}$ °K^{-1}), and became superconductive below 5.2°K.[6] Films containing 71 wt% Nb with $2r \simeq 20$ Å[7] (deposited at room temperature) had an activated conduction with activation energies ΔE increasing monotonically (Fig. 1, curve *a*) between 0.5×10^{-6} eV at 1.9°K and 4.4×10^{-3} eV at 300°K. This monotonic variation of