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The origin of a previously unassigned peak in the Brillouin spectrum of an oriented polymer film has been clarified. This peak is shown to be due to backscattering from a quasitransverse acoustic phonon from the reflected laser beam. Studies of this peak are expected to provide the information concerning the birefringence effect of the oriented film.

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Assignment of an Anomalous Peak in the Brillouin Spectrum of Oriented Polymer Films

By

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Prepared for Publication
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Assignment of an Anomalous Peak in the Brillouin Spectrum of Oriented Polymer Films

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ABSTRACT

The origin of a previously unassigned peak in the Brillouin spectrum of an oriented polymer film has been clarified. This peak is shown to be due to backscattering from a quasitransverse acoustic phonon from the reflected laser beam. Studies of this peak are expected to provide the information concerning the birefringence effect of the oriented film.

Brillouin light scattering has recently been developed as a technique for characterizing the elastic properties of oriented solid polymer samples.[1,2] The Brillouin spectrum of a uniaxially oriented thick polymer films generally contains four distinct inelastically scattered features, three of which have been assigned as scattering from the primary laser beam or from an internal reflection.[3] However, there is another feature present in the spectrum which we have referred to as an anomalous band that has been observed in studies carried out in our laboratory[1,4] and has also been noted by other workers.[5] This anomalous band is found in the spectra of oriented films, but not in the unoriented samples. The evolution of this peak with orientation has led to reports that for poly (ethylene terephthalate) (PET)[4] and poly (ethylene) (PE)[5] the anomalous band is caused by the inhomogeneity of the polymer structure and is a manifestation of the crystalline region which scatters light independently of the amorphous region. We have subsequently observed this anomalous band in oriented films of poly (propylene)(PP)[6] and poly (chlorotriflouroethylene)[2] (PCTFE). Independent amorphous and crystalline scattering in these polymers is less plausible since in PP, the crystalline regions in the oriented samples are not radically changed by orientation as they are in PET and in PE, and the PCTFE films are mostly amorphous with unstructured crystallinity. The purpose of this note is to provide a quantitative explanation for the anomalous band observed in polymer films.

When an unoriented film is oriented, the macroscopic symmetry changes from isotropic to cylindrical. This change of symmetry also affects the modes of sound propagation in the sample. The sound waves which propagate directly along the symmetry axes of the sample are purely compressional or purely shear in character. In polymers the pure compressional waves scatter light strongly while the pure shear waves scatter light only weakly. In directions away from the pure mode axes the longitudinal and shear modes mix, resulting in the quasi longitudinal (QL) and quasitransverse (QT) waves. The scattering intensity from both modes is prominent in the Brillouin spectrum in the oriented film.

The scattering from the QT is found at low frequencies, close to the laser frequency. In our earlier studies of polymer films using a 3-pass Fabry Perot interferometer [4] the QT scattering was covered by the Rayleigh wing, whereas a 5-pass interferometer which provides higher contrast has later revealed the QT scattering. [1,4]

Figure I is a Brillouin spectrum of an oriented PP film The peaks labelled 1 and 2 are scattering from the primary beam, ($\vec{q}_I$ in Fig. 2). The primary beam is partially reflected at the exit surface. The reflected beam gives rise to secondary scattering ($\vec{q}_{II}$ in Fig. 2). Peak number 3 in Fig. 1 is due to the secondary scattering from the QL mode along $\vec{q}_{II}$. Peak number 4 is the anomalous band.

For the scattering geometry shown in Fig. 2 where $\Sigma' = \Sigma'' = 45°$ the frequency shift of the peaks 1 and 2 is given by the expression:[3]

$$\nu_I = \frac{V_s{}^I \sqrt{2}}{\lambda_i} \tag{1}$$

where $V_s{}^I$ is the sound velocity of the waves along $\vec{q}_I$ and λ_i is the wavelength of the laser radiation. The frequency shift of the backscattered QL peak 3 is given by:

$$\nu_{II} = \frac{V_s{}^{II} 2n}{\lambda_i} \tag{2}$$

where n is the refractive index of the medium along $\vec{q}_{II}$ By rotating the film in the scattering plane so that the direction of the scattering vector is varied, the sound velocity of the QL and QT waves can be measured in different directions in the film plane. We define the angle α as the angle between the orientation (z-) axis and the primary scattering vector, $\vec{q}_I$. The x and y axes are perpendicular to z, with x in the film plane. We will now establish that peak No. 4 shown in Fig. 1 is the backscattering from the QT mode along $\vec{q}_{II}$. This mode shall hereby be designated as the BSQT mode. We first derive an expression to determine the direction of the backscattering vector $\vec{q}_{II}$ in the film coordinates as a function of the rotation angle α.

The angle ξ is the angle of the secondary beam to the film normal, as illustrated in Fig. 2. From Snell's law this is given by ($\Sigma' = 45^\circ$):

$$\xi = \sin^{-1}\left(\frac{.707}{n}\right) \tag{3}$$

The incident and scattered wavevectors for the backscattering geometry are:

$$\vec{\kappa}_i = \frac{2\pi\, n}{\lambda} \begin{pmatrix} \sin\alpha\,\sin\xi \\ -\cos\xi \\ \cos\alpha\,\sin\xi \end{pmatrix} \tag{4a}$$

$$\vec{\kappa}_s = \frac{2\pi\, n}{\lambda} \begin{pmatrix} -\sin\alpha\,\sin\xi \\ \cos\xi \\ -\cos\alpha\,\sin\xi \end{pmatrix} \tag{4b}$$

where in Eqs. (4a) and (4b) we have neglected the birefringence effect. From the conservation of momentum, we have found the scattering vector as

$$\vec{q}_{II} = \frac{4\pi\, n}{\lambda} \begin{pmatrix} \sin\alpha\,\sin\xi \\ -\cos\xi \\ \cos\alpha\,\sin\xi \end{pmatrix} \tag{5}$$

The angle η (shown in Fig. 2) is the angle between $\vec{q}_{II}$ and the z axis of the film and is given by

$$\cos \eta = \frac{\cos \alpha \sin \xi}{[(\cos \alpha \sin \xi)^2 + (\sin \alpha \sin \xi)^2 + (\cos \xi)^2]^{\frac{1}{2}}} \quad . \qquad (6)$$

It is apparent from this expression that as α approaches 90° the scattering vector $\vec{q}_{II}$ becomes perpendicular to the z axis, a pure mode direction. Since the scattering from the pure transverse modes is weak in most polymers, we would expect that the BSQT peak will fade from the spectrum as α approaches 90°. This is consistent with the experimental results obtained in all cases studied to this point, both in our laboratory and in others.[5]

To calculate the frequency shift of the BSQT mode as a function of α we require the QT sound velocity at various angles of η in the film. The determination of QL and QT sound velocities has been described previously.[1,2] Shown in Fig. 3 are the QL and QT sound velocities for a *poly(propylene)* (R_s=7.26) film as a function of angle η . The angle η is determined by using Eq. (6). Knowing the QT sound velocity as a function of angle η, we can determine the QT frequency shift as a function of α according to Eqs. (2) and (6). The calculated and experimental frequency shift for the BSQT mode in the R_s=7.26 film are plotted in Fig. 4. The agreement between calculation and experiment is fairly good. It should be noted that in this calculation, we have not included the effect of optical birefringence. However, in order to scale the calculated frequency shifts match the experimental result, we found it necessary to use the value n = 1.55 in the calculation for the highly oriented film. This is slightly larger than the isotropic film index of 1.49. Thus, the effect of optical birefringence plays a role in affecting the result. It appears that careful measurements of the BSQT and the back scattered QL frequency provide a potentially valuable method for investigating the effect of birefringence on the oriented polymer films.

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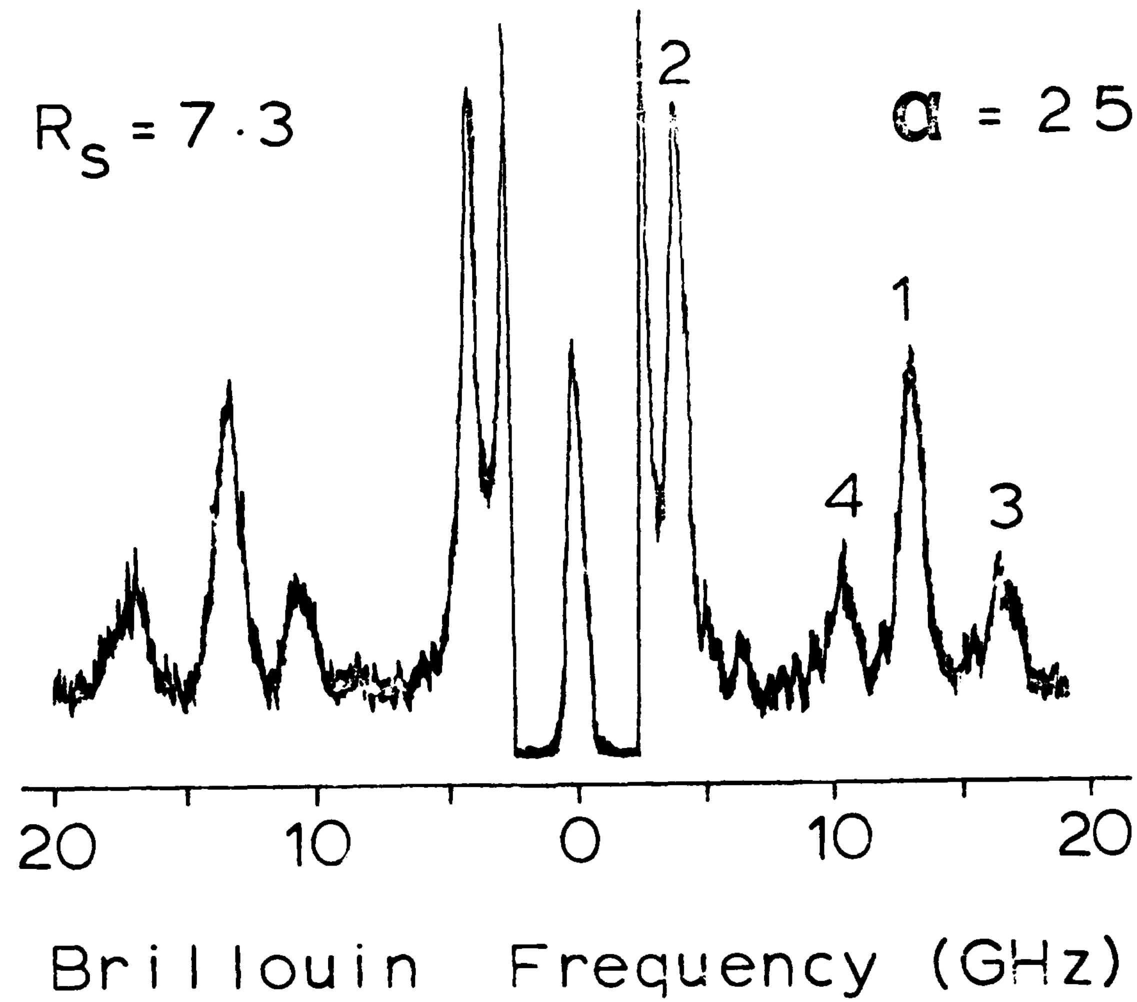
Figure Captions

1. The Brillouis spectrum of a polypropylene film; draws ratio 7.3, where $\alpha = 25^{o}$. The peaks are assigned as 1. QL. scattering from $\vec{q}_I$, 2. QT scattering from $\vec{q}_{II}$, 3. QL. scattering from $\vec{q}_I$, 4. QT scattering from $\vec{q}_{II}$.

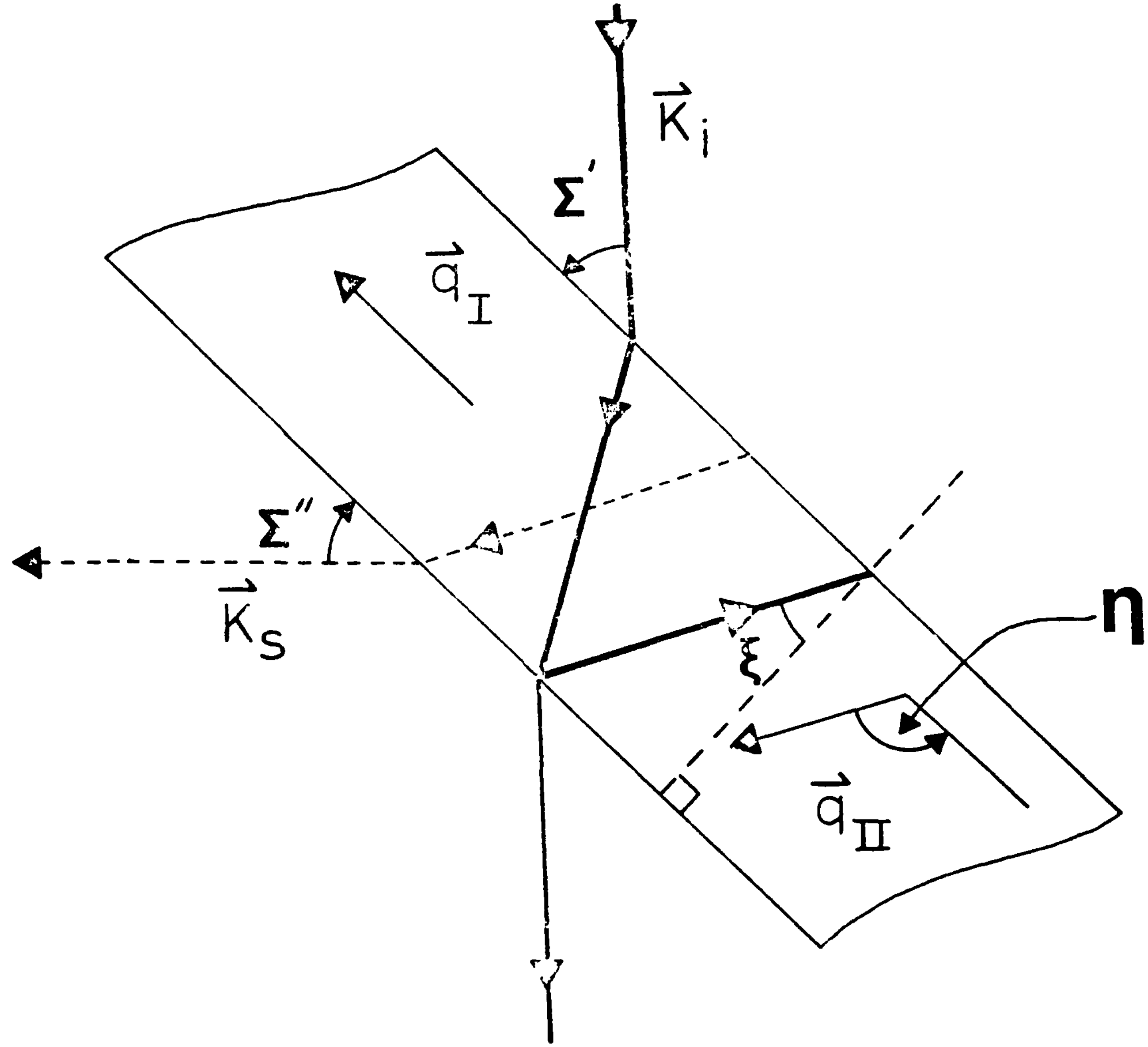
2. Diagram of the scattering geometry showing the orientation of $\vec{q}_I$ and $\vec{q}_{II}$. The view is from the top of the film, across the film thickness.

3. The QL and QT sound velocities as a function of η in the $R_s = 7.3$ polypropylene film.

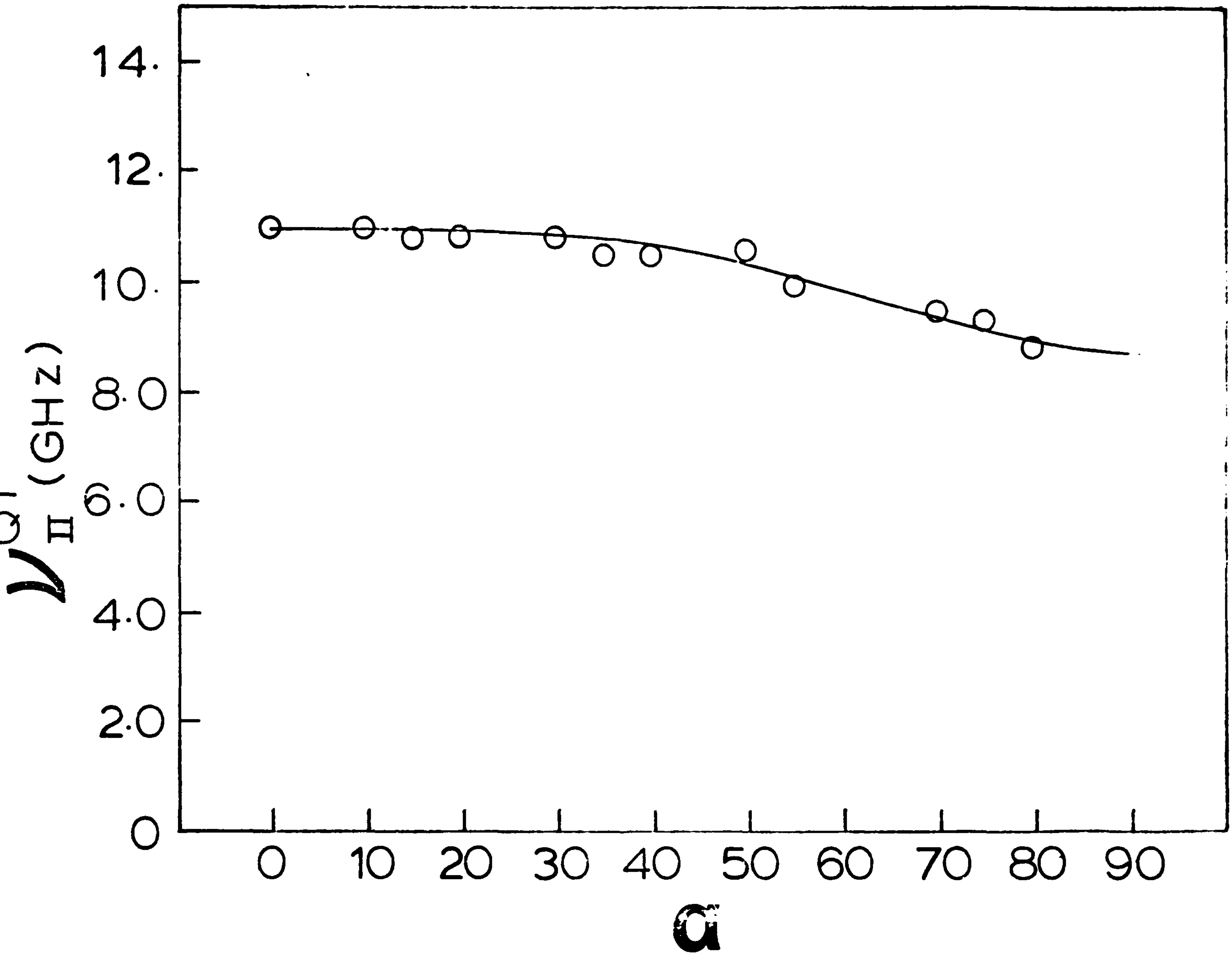
4. The Brillouin frequency shift of the BSQT peak, calculated for different angles of α in the $R_s = 7.3$ film O - experimental points —— - calculated frequency shift.



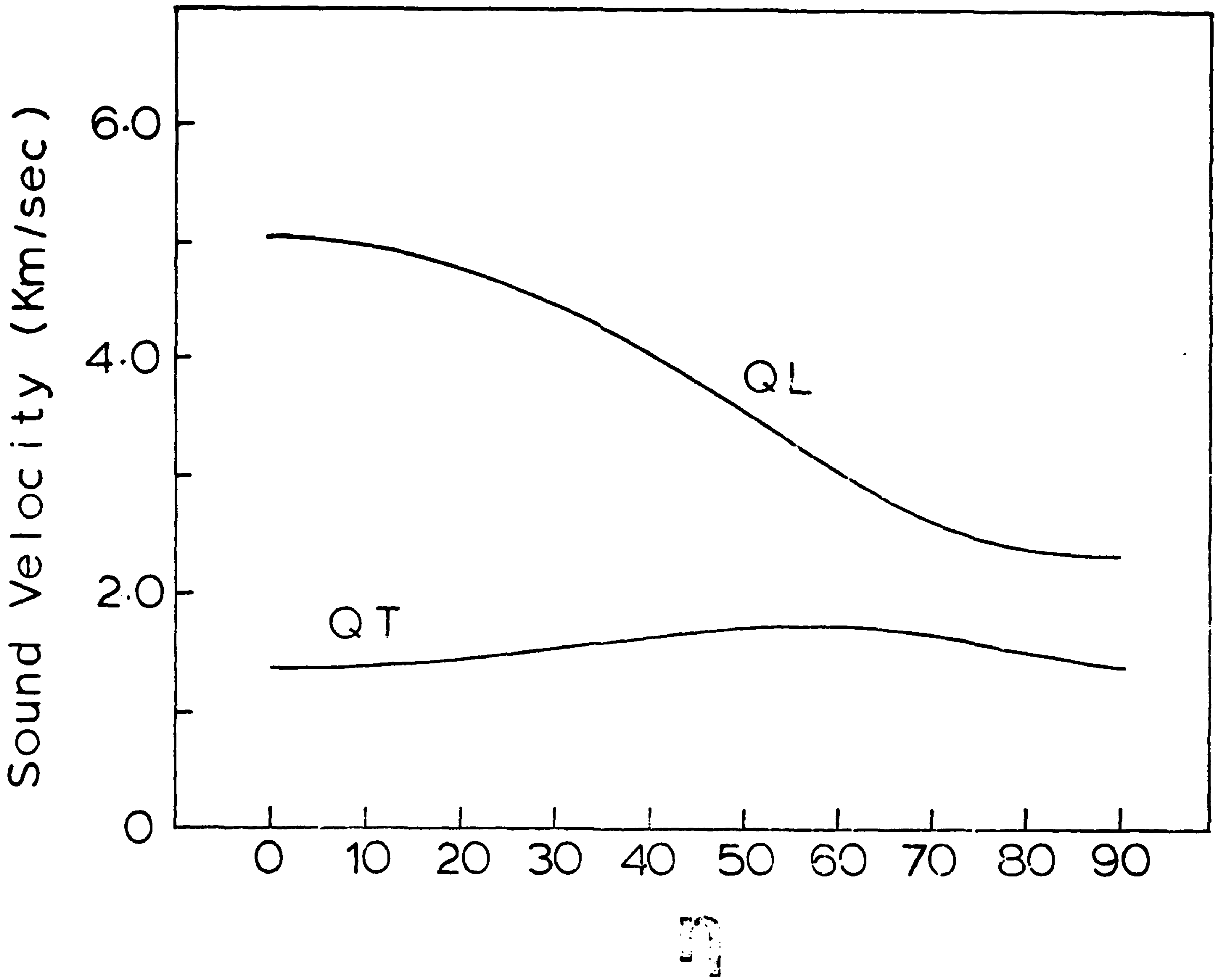
$R_s = 7.3$
$\alpha = 25°$
2
1
4
3
20
10
0
10
20
Brillouin Frequency (GHz)



$\vec{K}_i$
Σ'
$\vec{q}_I$
Σ''
$\vec{K}_S$
ξ
η
$\vec{q}_{II}$



ν_{II}^{QT} (GHz)
14.
12.
10.
8.0
6.0
4.0
2.0
0
0
10
20
30
40
50
60
70
80
90
a


Sound Velocity (Km/sec)
0
2.0
4.0
6.0
QL
QT
0
10
20
30
40
50
60
70
80
90
η

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