We conclude with a physical description of the modes of oscillation. If the velocity of sound (8) is inserted in (5), we find that $\delta\rho_S/\rho_S \approx (1+\Lambda)^{-1}(\delta N/N_0)$. Thus the relative bunching of the $He^3$ is of the same order of magnitude as the relative density changes in the $He^4$: The superfluid and the normal fluid respond in roughly the same way to the sound. On the other hand, if the velocity of the $He^3$-like modes is inserted into (5), $s^2$ may be dropped in comparison with $\bar{s}^2$, and we find that $\delta\rho_S/\rho_S \approx -(1+\Lambda')(N_0 m_0^*/\rho_S)(\delta N/N_0)$. That is, the relative density changes in the superfluid are quite negligible in comparison with the $He^3$ bunching. This is reasonable, for we would expect that the $He^3$-like modes would be propagated mainly by density changes in the $He^3$ and not by the superfluid. However, because of the much larger density of $He^3$, the absolute value of the density change $\delta\rho_S$ is the same order of magnitude as $m_0^*\delta N = \delta\rho_n$,[6] the normal density change. Actually, the $He^3$-like modes are rather similar to second sound in pure $He^4$. This is because the density changes in the normal fluid are of the same order of magnitude, and of opposite phase to the density changes in the superfluid: $\delta\rho_S + \delta\rho_n \approx -\Lambda'\delta\rho_n$.

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[6]The terms "normal fluid" and "superfluid" have been used very imprecisely here. In fact, the definitions for normal fluid and superfluid density given here agree with the usual definition (see Ref. 2, for example) only if interactions between the $He^3$ quasiparticles are neglected. However, these are useful concepts for a qualitative understanding of the modes of propagation.

## PRESSURE-INDUCED PHONON FREQUENCY SHIFTS IN LEAD MEASURED BY INELASTIC NEUTRON SCATTERING*

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Phonon frequency shifts due to the change of temperature have already been measured for several materials, in particular for lead.[1] These shifts reflect the deviation of the crystal potential from that assumed in the harmonic approximation. This deviation can also be explored by artificially changing the relative positions of the atoms in the crystals by application of external forces.

We have measured by the method of neutron spectrometry the frequency shifts of six selected phonons in lead due to the application of a hydrostatic pressure of 3000 atm. The measurements were done on a conventional triple-axis spectrometer in a constant-$Q$ mode of operation.[2] The scattering chamber for 3000 atm and for a sample of 30 mm diameter and 65 mm length is described in detail elsewhere.[3]

The positions of the six selected phonons are shown in Fig. 1 as circles in the dispersion curves of lead[4] for the directions $[\zeta 0 0]$ and $[\zeta \zeta \zeta]$. Figure 2 shows the results of a typical shift measurement. Because of the low phonon energy, the phonon peak is superimposed on a falling background due mainly to elastic scattering in the sample and in the wall of the pressure chamber. For the evaluation of the shift the center of a peak was defined by the intersection of two straight lines fitted to the flanks of the peak. The assumption was made that the shape of the phonon peak is not altered by the pressure. This assumption is not contradicted by any of our measurements. The influence of a falling background on the shift is eliminated by this evaluation method as long as the background is approximately linear.

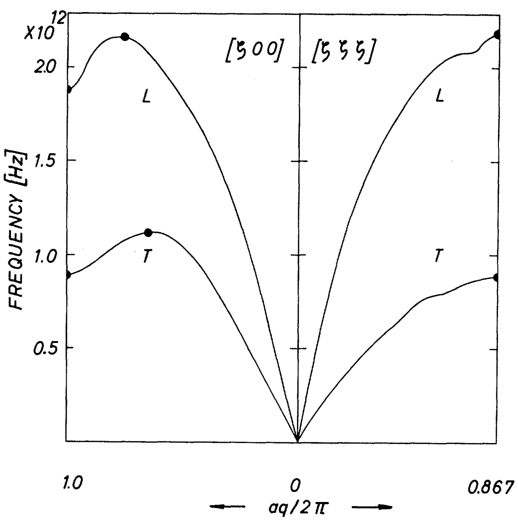


FIG. 1. Dispersion relations in the directions [ζ 0 0] and [ζ ζ ζ] of lead according to Brockhouse et al.[4] The circles indicate the positions of the six phonons measured in the present work.

The statistical accuracy of the measured frequency shifts $\Delta\omega$ was evaluated according to formula (1) which is a slight generalization of a formula used by Brockhouse et al.[4]:

$$\delta(\Delta\omega) = [2(N+B)/n]^{1/2} d\omega/dN, \tag{1}$$

where $N$ is the mean number of true (one-phonon) counts per point, $B$ is the mean number of background counts per point, and $n$ is the number of points in a peak. The magnitude of several other, nonstatistical uncertainties (such as nonlinearity of background and the ambiguity in the straight-line fitting) were estimated and were found to be negligible against the statistical error.

The results of the measurements are given in Table I in terms of the quantity $\gamma_{qj}$, the microscopic Grüneisen parameter of the mode $(q,j)$, which is defined by

$$\gamma_{qj} = -d\ln\omega_{qj}/d\ln V \tag{2}$$

where $V$ is the crystal volume. In Fig. 3 these $\gamma_{qj}$ are compared with $\gamma$'s derived from temperature-induced phonon energy shifts of lead.[1] The uncertainties of the latter (shaded areas in Fig. 3) have been estimated for the [ζ 0 0] phonons from the scatter of the points in the dispersion curves of Ref. 1. For the [ζ ζ ζ] phonons the uncertainty is probably of the same

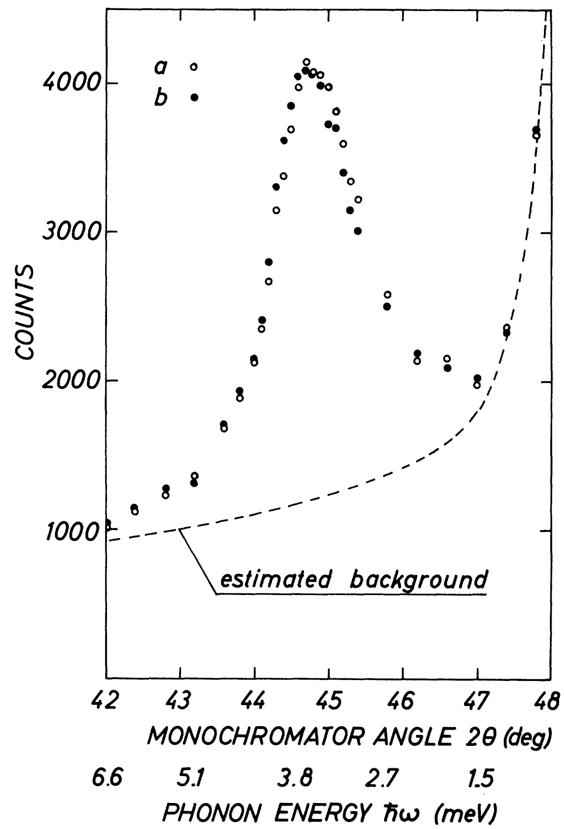


FIG. 2. Typical measurement of a phonon frequency shift: (a) peak at zero pressure; (b) peak at 3000 atm.

order of magnitude. Within these errors, agreement with our $\gamma$'s is found except in the case of the two transversal [ζ 0 0] phonons. Also shown in Fig. 3 is the value of the macroscopic Grüneisen constant $\gamma_G = 2.48$ calculated according to

$$\gamma_G = \alpha B_T V/C_v, \tag{3}$$

where $\alpha$ is the volume coefficient of thermal expansion, $B_T$ is the bulk modulus, $C_v/V$ is the heat capacity per unit volume of the crystal. In the microscopic theory of the equation of state of solids $\gamma_G$ is a weighted average of the microscopic $\gamma_{qj}$.[5] The weighting factors are the contributions $(C_v)_{qj}$ of all the modes to the heat capacity $C_v$. In the limit of classically high temperatures, where $(C_v)_{qj}$ is equal to the Boltzmann constant $k$ for all modes, $\gamma_G$ is the simple average of the $\gamma_{qj}$. In the case of lead this should be true already at room temperature because of its low Debye temperature ($\theta_0 = 94.5°K$[6]). It can be seen in Fig. 3 that at

Table I. Observed zero-pressure phonon energies $\hbar\omega_{qj}$, relative phonon energy changes[a] $[\Delta(\hbar\omega_{qj})]/\hbar\omega_{qj}$, and derived microscopic Grüneisen parameters $\gamma_{qj}$.

| Phonon | | | Results | | |
|---|---|---|---|---|---|
| Direction of propagation | Polarization | $aq/2\pi$ | $\hbar\omega_{qj}$ (meV) | $\frac{\Delta(\hbar\omega_{qj})}{\hbar\omega_{qj}}\times 100$ | $\gamma_{qj}$ |
| $[\xi\,\xi\,\xi]$ | T | 0.867 | $3.63 \pm 0.06$ | $1.82 \pm 0.21$ | $2.66 \pm 0.30$ |
| $[\xi\,\xi\,\xi]$ | L | 0.867 | $9.24 \pm 0.10$ | $0.64 \pm 0.30$ | $0.91 \pm 0.43$ |
| $[\xi\,0\,0]$ | T | 1.0 | $3.64 \pm 0.23$ | $2.73 \pm 0.55$ | $3.86 \pm 0.78$ |
| $[\xi\,0\,0]$ | T | 0.65 | $4.41 \pm 0.14$ | $0.68 \pm 0.43$ | $0.97 \pm 0.62$ |
| $[\xi\,0\,0]$ | L | 1.0 | $7.70 \pm 0.30$ | $0.75 \pm 0.97$ | $1.07 \pm 1.39$ |
| $[\xi\,0\,0]$ | L | 0.75 | $8.96 \pm 0.25$ | $1.61 \pm 0.92$ | $2.29 \pm 1.31$ |

[a] $\Delta(\hbar\omega_{qj}) = \hbar\omega_{qj}(3000\text{ atm}) - \hbar\omega_{qj}(0\text{ atm})$.

the Brillouin-zone boundaries in the directions $[\xi\,0\,0]$ and $[\xi\,\xi\,\xi]$ the $\gamma_{qj}$ values are larger for transverse than for the corresponding longitudinal modes. For the two in-zone modes in the $[\xi\,0\,0]$ direction, which can be compared only if a small difference in their $q$ values is neglected, the contrary seems to be true: $\gamma_{qj}$ of the longitudinal mode is larger than that of the transverse mode.

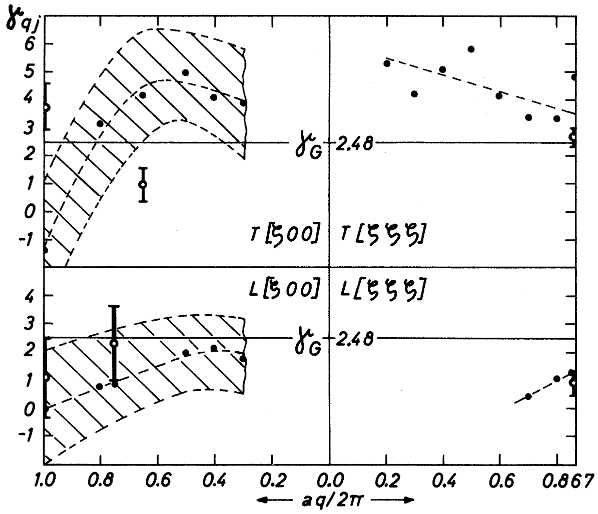


FIG. 3. Comparison of microscopic Grüneisen parameters $\gamma_{qj}$ derived from the present measurements (open circles) with those derived from the temperature-induced phonon energy shifts of Ref. 1 (closed circles). The shaded areas indicate uncertainties estimated from the scatter of points in Fig. 5 of Ref. 1.

Finally, we note that the determination of pressure-induced phonon energy shifts should be of relevance not only to the microscopic theory of the equation of state but also to an examination of the quasiharmonic approximation (as pointed out, e.g., by Daniels[7]) and perhaps to theories aimed at the calculation of phonon frequencies from first principles.

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