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Temperature dependence of lattice dynamics in lead

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Abstract. Inelastic neutron scattering measurements on lead have been performed at six temperatures from 4.2 K up to 245 K using the PRISMA spectrometer installed at the ISIS spallation neutron source at the Rutherford Appleton Laboratory, UK. With the present experiment we wish to emphasize the importance of measuring the phonon response function over a wide energy range especially when studying temperature-related phenomena.

1. Introduction

In the last thirty years inelastic neutron scattering has been widely employed to study the lattice dynamics of crystals, and standard triple-axis spectrometers [1] have proved to be an extremely powerful tool to investigate phonon dispersion relations. Generally the main concern of experimental measurements has been the determination of dispersion relations, although in some cases the lineshape of the phonon peaks has also been the subject of study.

Lead has always been considered a good prototype for the study of lattice dynamics as it shows many interesting features. Different aspects of the dispersion relations of lead have been investigated by several authors since 1960 [2–6]. In [2] and [3] the main concern was an extensive analysis of the phonon dispersion relations, although the presence of Kohn anomalies as well as the temperature dependence of the phonon lifetimes was also investigated. More recently, the effect of the superconducting transition on the phonon lifetime has been studied with contradictory results [4–6]. Indeed in [5] it has been reported that an appreciable change in the lifetime of some phonon modes occurs at the superconducting transition ($T_c = 7.2$ K). On the other hand no such effect was observed in the experiment reported in [6] where a sharper resolution was employed. The simplest explanation of these contradictory results has been that there was some error in the interpretation of the data in [5]. However, an alternative interpretation of these results can be proposed as follows. Considering that the effect observed in [5] occurs at temperatures close to the superconducting transition, it can be assumed that the electron–phonon interaction (EPI) is responsible since the temperature dependence of the anharmonic contribution is too small to make the anharmonic contribution of importance in this temperature range. At low temperature the phonon self-energy

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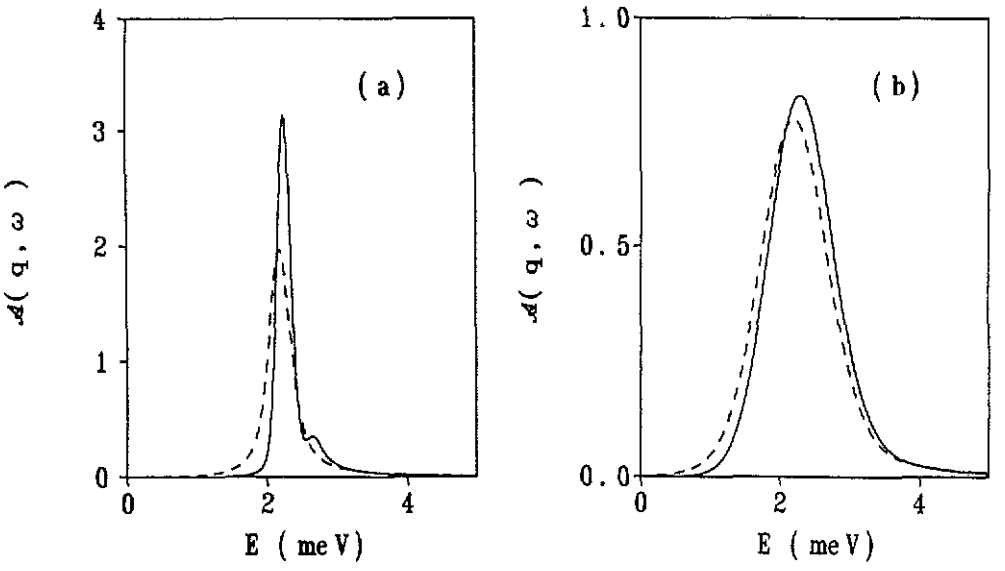

Figure 1. Phonon response function $A(q, \omega)$ versus energy, calculated according to (2) at $\omega_q = 2.2$ meV and convoluted with a Gaussian function having FWHM = 0.2 meV (*a*) and 1 meV (*b*). Full curve: superconducting phase; broken curve: normal phase. The superconducting gap was assumed to be $2\Delta = 2.7$ meV.

$\Sigma(\omega)$, related to the EPI, has a simple analytic expression [7] that can be used to calculate the one-phonon response function $A(q, \omega)$ for a given *bare* phonon frequency ω_q:

$$A(q, \omega) = -(1/\pi)\,\mathrm{Im}(\omega^2 - \omega_q^2 - \Sigma(\omega))^{-1}. \tag{1}$$

In order to get some insight into the effect of the superconducting transition on the phonon lineshape when ω_q is close to the superconducting gap, we have calculated $A(q, \omega)$ using a self-energy reasonably suited for lead. Some typical results are shown in figure 1, where the effect of the experimental resolution has been taken into account by convoluting the calculated one-phonon cross section with a Gaussian function. A sharp resolution [6] has been simulated using a full width at half-maximum (FWHM) of 0.2 meV, while the broad resolution of [5] was simulated using a FWHM of 1 meV. As can be seen from figure 1, the transition from the superconducting to the normal phase affects both the principal phonon peak and the tails. Such an effect is still present when using the broader resolution in the calculation, since the integrated intensity in the tail is an appreciable proportion of the total integrated intensity. Indeed, the response function exhibits changes over an energy range in excess of 2 meV, whereas the scans performed in [6] were always shorter than 1 meV. Furthermore, we note that the observed energy shift with temperature can be appreciable even when a relatively broad resolution is employed. An energy shift similar to that deduced from the present model has been observed in [8] for the case of Nb_3Sn, for which it is known that the effect of the EPI is quite important.

The behaviour of $A(q, \omega_q)$ found using this simple model suggests that a detailed investigation of the one-phonon cross section over a relatively wide energy range would be essential in order to interpret the lattice dynamics when the temperature is close to that of a transition or when one is interested in obtaining information on the phonon

self-energy. Since the measurement of the tails of the one-phonon cross section is obscured by the presence of the more diffuse spectrum due to multi-phonon contributions, long scans are also important in order to estimate these other contributions.

Although in principle the one-phonon cross section can be studied easily using a standard triple-axis spectrometer, which can cover almost all of the region of interest in energy–momentum space, in practice this approach is too time consuming. Therefore, in order to carry out an extensive study of the phonon response function in lead we have used the time-of-flight technique.

Recently it has been shown [9, 10] that a properly designed instrument can be employed on a pulsed neutron source to achieve accurate measurement of the inelastic scattering from single crystals. The advantage of the time-of-flight technique, using a white incident neutron beam, is the simultaneous measurement of a wide range of energy transfers. The PRISMA spectrometer installed at the spallation neutron source ISIS represents a facility that is particularly suited to the study of phonon line-shapes. The present resolution ranges from 0.7 meV to 1.5 meV for energy transfers of up to 50 meV.

To perform an initial experimental analysis of a phonon response function over a wide energy range using the time-of-flight technique, we selected lead as the prototype for this sort of experiment. This choice was also influenced by the discrepancies found in the results reported in [5, 6] and described above, and by the fact that lead shows strong anharmonic behaviour [2, 4], so an appreciable temperature dependence of the phonon response function is expected.

2. Experiment and results

The experiment has been performed at the ISIS pulsed source (UK) using the PRISMA spectrometer [9, 10]. The variation with energy of the incident beam intensity was measured using a monitor in front of the sample. In all of the scans performed, 15 independent Ge (111) analysers and ^{3}He detectors were employed. The collimations used were 0.7° (moderator–sample), 1° (sample–analyser) and 1.4° (analyser–detector). The sample was a cylinder, 2.5 cm in diameter and 5 cm in height with its vertical axis parallel to the [001] direction. The mosaic spread of the crystal was 0.3° with a uniform rocking curve. The sample was mounted in a standard-orange cryostat where its temperature could be held constant to within ±0.2 K. Since the superconducting transition temperature is 7.2 K while the Debye temperature is about 80 K, the experimental data were collected at 4.2 K, 9 K, 45 K, 107 K, 145 K and 245 K. The measurements at different temperatures were performed with the sample *in a fixed position* [10]. The final energies selected by the different analysers were chosen in order that the scan direction be along the $[1\bar{1}0]$ direction through the (400) reciprocal lattice point, the incoming beam direction being along the $[1\bar{1}0]$ direction, as shown in figure 2. In the present configuration the $(\zeta\zeta 0)$L and the $(\zeta\zeta 0)T_1$ branches were accessible, while the $(\zeta\zeta 0)T_2$ branch had zero cross section because its polarization vector was perpendicular to the momentum transfer. A second scan configuration with slightly different final energies was employed at 4.2 K and 9 K to get additional data around the superconducting transition. The (q, ω) region spanned in the present experiment is shown in figure 3.

All data collected have been corrected for a background independent of the time of flight and normalized to the incoming spectrum. No correction for the analyser reflectivity has to be performed because the final energy is constant. However, to account for the different reflectivities of the analysers and also for possible differences in the neutron

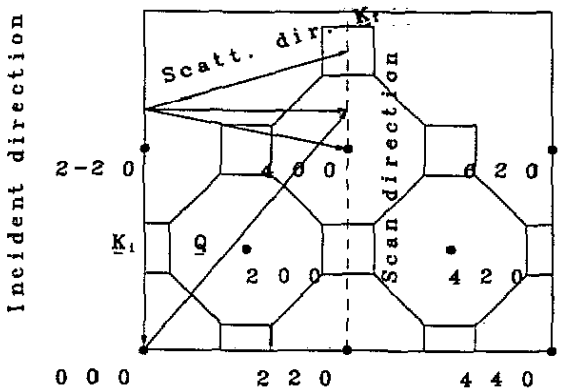

Figure 2. Scan geometry superimposed on the Brillouin zone boundaries.

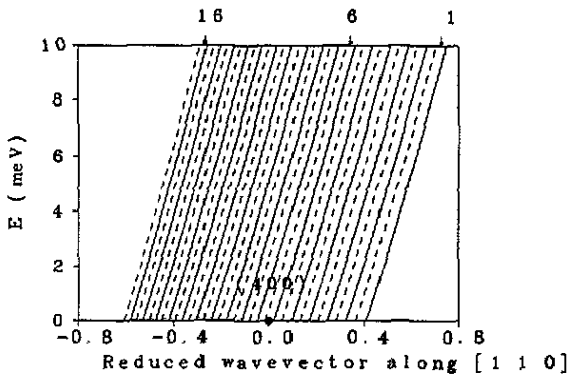

Figure 3. The (q, E) region spanned in the present experiment. The full and broken lines indicate the time-of-flight trajectories along which data were measured for two different spectrometer settings. Counter numbers are shown to identify the region covered around the (400) reflection that is seen by detector 6.

optics, the data from different detectors have been normalized to the scattering from a vanadium sample that is an incoherent scatterer. As an example, some of the data are shown in figures 4 (4.2 K and 9 K) and 5 (45 K and 145 K) as a function of the energy transfer.

Looking at the temperature dependence of the neutron cross section, the high-energy contribution (4 meV to 9 meV) found in the spectra at 45 K and 145 K is due to sample scattering and, in view of its strong temperature dependence, can be safely identified as a multi-phonon contribution. A calculation of the multi-phonon cross section, in the incoherent approximation [11], has been performed using the density of states deduced in [3]. The results of this calculation are shown in figure 5 where it can be seen that the calculation accounts reasonably well for the multi-phonon tail in the experimental data. Some discrepancy is, however, present at the positive energy side, thus suggesting some anharmonic behaviour. Although the multi-phonon contribution is small it was subtracted from the experimental data in order to better approximate the one-phonon cross section in the tail region.

Of course in view of the relatively broad resolution of the present experiment, the shape of the neutron cross section is dominated by resolution effects even though an

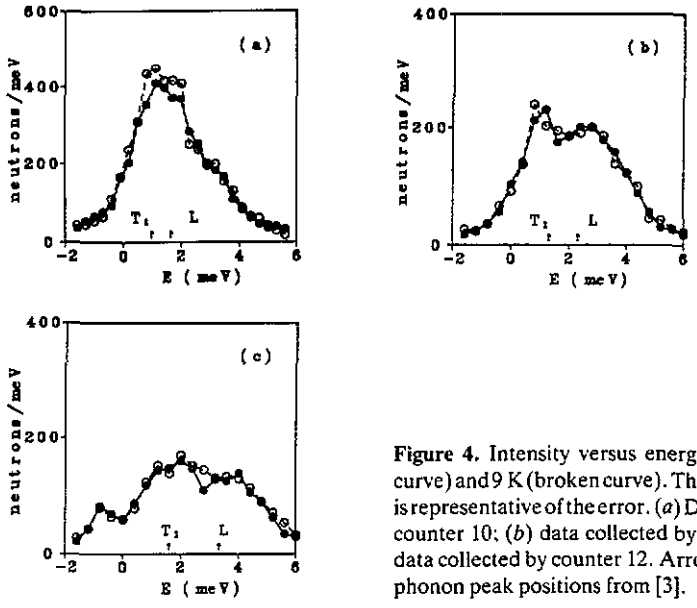

Figure 4. Intensity versus energy at 4.2 K (full curve) and 9 K (broken curve). The size of the dots is representative of the error. (*a*) Data collected by counter 10; (*b*) data collected by counter 11; (*c*) data collected by counter 12. Arrows indicate the phonon peak positions from [3].

overall decrease in the energy of the phonon peaks with increasing temperature is seen. We have deduced the amount of reduction in the phonon energy by comparing the one-phonon response function $A_4(q, \omega)$ at the lowest temperature (4.2 K) with $A_T(q, \omega)$ measured at temperature T and taking the minimum of the following mean-square difference:

$$\Delta^2 = \sum_1^N {}_i \, |A_4(q, \omega_i) - A_T(q, \alpha\omega_i)|^2 \, W_i \tag{2}$$

where ω_i are the experimental frequencies at which the response function has been measured, W_i are weights chosen according to the experimental errors and α is a parameter that measures the energy change as a function of temperature. In figure 6 we plot the average value of α deduced from our energy-loss scans as a function of temperature. As the variations of α around the average value are relatively small, we can say that the response function has an almost uniform contraction with temperature in the q and ω ranges analysed. A similar conclusion about the peak positions can be drawn from the data of [4], which are also shown in figure 6.

Of course, the parameter α gives only a measure of the overall phonon energy shift due to the lattice parameter change, anharmonic contribution and EPI. However, a closer examination of $A(q, \omega)$ suggests more complex effects. In the case of the low-temperature phonons, small changes in the experimental peaks can be seen when increasing the temperature from 4.2 K to 9 K. From the data shown in figure 4(*a*) an increase of about 0.1 meV of the T_1 peak energy can be estimated. This shift is higher than that expected for anharmonic and volume contributions [4, 12]. Moreover, it is interesting to observe that a careful analysis of the data presented in [6], where a much sharper resolution was employed, results in a similar shift and systematic changes in the tails of the peak, although the energy range was too small to conclude more than this.

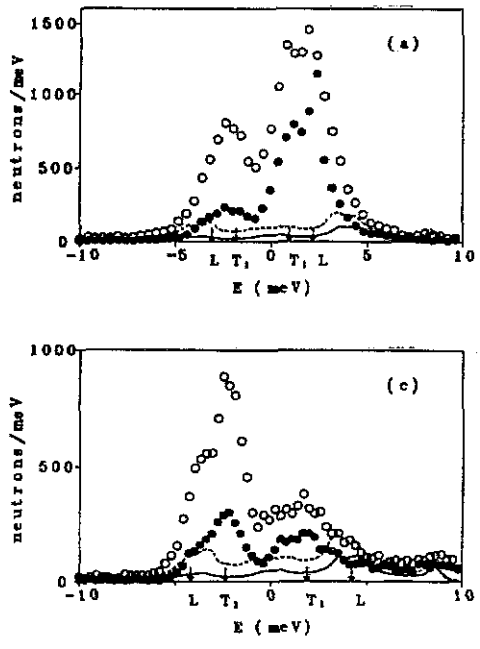

Figure 5. Intensity versus energy at 45 K (full circles) and 145 K (open circles). Multi-phonon contributions at 45 K (full curve) and 145 K (broken curve) are also shown. (*a*) Data collected by counter 10; (*b*) data collected by counter 2; (*c*) data collected by counter 3. Arrows indicate the phonon peak positions from [3].

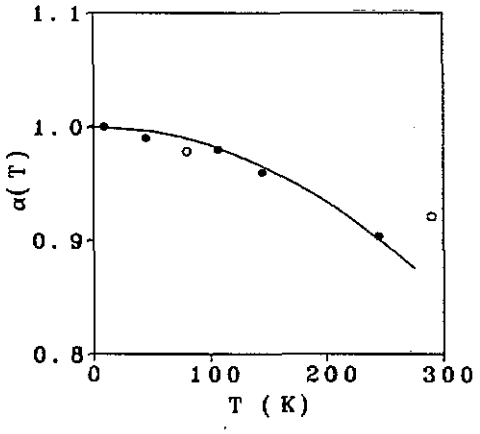

Figure 6. The average value of the parameter α (see text) versus temperature: present data (full circles); data from [4] (open circles). The full curve is a guide for the eye.

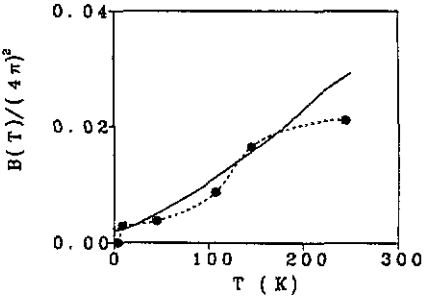

Figure 7. The thermal parameter $B(T)$ versus temperature: present data (full circles); theoretical curve calculated in the quasi-harmonic approximation (full curve). The size of the dots is representative of the error. The broken curve connecting dots is a guide for the eye.

To obtain further insight into the softening of the phonon energies with increasing temperature, we determined the Debye–Waller factor $\exp[-2W(Q)]$, by studying the intensity of the (400) Bragg peak. This intensity was measured on the tail of the crystal rocking curve, as seen by counter nine, to minimize the effect of secondary extinction, which is quite large because of the size of the sample studied. A small correction was

made to take into account both the effect of thermal expansion, which affects the experimental intensity by changing the reflectivity, and the effect of instrumental resolution. As the Debye–Waller factor at 4.2 K is due to zero-point motion only, the temperature-dependent part of $\exp[-2W(\boldsymbol{Q})]$ can be deduced from the data presented here. As usual, we can write:

$$\exp[-2W(\boldsymbol{Q})] = \exp[-2(B(T) + B_0)(\sin\theta_B/\lambda^2)^2] \tag{3}$$

where θ_B is the Bragg angle and λ is the neutron wavelength. B_0 is a constant related to the zero-point motion and $B(T)$ is the temperature-dependent contribution. By assuming B (4.2 K) = 0, we deduced the values of $B(T)$ that are shown in figure 7, for comparison with the results of a calculation [11] performed in the quasi-harmonic approximation. In particular, the density of states from [4] that is employed in this calculation was corrected for the overall temperature dependence of the phonon frequencies as shown in figure 6. The theoretical curve shown in figure 7 fits the experimental data reasonably well although a strong disagreement is found at the highest temperature where the experimentally determined $B(T)$ is smaller than the theoretical one. This behaviour indicates that the anharmonicity produces a direct effect on the Debye–Waller factor in addition to that through the change of the density of states. In an anharmonic system the exponent of the Debye–Waller factor can be written as follows [13]:

$$W(\boldsymbol{Q}) = \langle(\boldsymbol{Q}\cdot\boldsymbol{u})^2\rangle - \tfrac{1}{4}[\tfrac{1}{3}\langle(\boldsymbol{Q}\cdot\boldsymbol{u})^4\rangle - \langle(\boldsymbol{Q}\cdot\boldsymbol{u})^2\rangle^2] + \ldots \tag{4}$$

where $\boldsymbol{u}$ is the nuclear displacement. The quantity within square brackets is zero for a harmonic system, while it gives a finite contribution when anharmonicity is present, as is the case for lead even in the temperature range that we have analysed. It should be noted that this term is always negative in agreement with the experimental findings.

More notably, there is an appreciable change of $B(T) - B_0$ between 4.2 K and 9 K. Such a change cannot be accounted for by $B(T)$ since, as $B(T)$ is extremely small in this temperature range, this would require very strong changes in the phonon density of states. On the other hand it is reasonable to assume that a small but rather abrupt change in the phonon density of states, due to the softening introduced by the EPI, is present between 4.2 K and 9 K, so B_0 will be changed by an appreciable amount. In particular, the superconducting transition could be responsible for the abrupt increase of B_0 when increasing the temperature through 7.2 K. Below the superconducting transition the imaginary part of the self-energy decreases when the phonon energy is less than the superconducting gap because electron–hole creation, through the EPI [7], is not possible. The decrease of the imaginary part of the self-energy when the phonon energy is small results in a decrease of the renormalized phonon density of states and hence of the zero-point contribution to the Debye–Waller factor.

In conclusion we can say that the use of standard triple-axis spectroscopy can limit the possibility of analysing in detail the effect of the phonon self-energy, such as the effect of the EPI or phase transitions [14]. The EPI produces a shift and a broadening of the phonon peak as a first-order approximation only. Indeed, such an interaction, as well as the phonon–phonon interaction, is expected to produce an appreciable change in the line-shape [15, 16]. As was shown by the simple model used earlier, a broad distribution appears together with a rather sharp peak.

Finally, the data presented show that an appreciable amount of anharmonicity is observed in a wide energy range and they allow for the determination of the overall contraction of the phonon energy distribution as the temperature is increased.

Acknowledgment

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