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Alois Loidl, J. Daubert, E. Schedler

Angaben zur Veröffentlichung / Publication details:

Loidl, Alois, J. Daubert, and E. Schedler. 1976. "Phonon dispersion in NaF in the region between zero and first sound, measured by inelastic neutron scattering." *Journal of Physics C: Solid State Physics* 9 (2): L33–37. https://doi.org/10.1088/0022-3719/9/2/002.

Phonon dispersion in NaF in the region between zero and first sound, measured by inelastic neutron scattering†

A Loidl‡, J Daubert‡ and E Schedler§

‡ Institut für Kernphysik der Universität Frankfurt. Frankfurt am Main 90. W Germany

§ Institut Laue–Langevin. BP 156 Centre de Tri, 38042 Grenoble Cedex, France

Abstract. This is the first inelastic neutron scattering experiment covering the transition region between zero and first sound. Measurements in NaF were performed in a wavevector region $0{\cdot}06 \leqslant q/q_{max} \leqslant 0{\cdot}25$ at 295, 500, 600 and 700 K. The experimental data cover the zero-sound region at room temperature and the transition region near first sound at 700 K. We show that it is possible to describe the frequency dependence of the sound velocities by use of an averaged thermal-phonon lifetime. The isothermal elastic constants and the averaged phonon lifetimes are determined at each temperature, and the zero-sound elastic constants at room temperature.

In anharmonic crystals, the mode of propagation of sound waves changes at sufficiently low frequencies depending on the relation between the applied frequency Ω and the averaged inverse lifetime Γ of the thermal phonons in the crystal. A microscopic theory (Cowley 1967, Niklasson 1972) shows that low-frequency waves with $\Omega \ll \Gamma$ travel at adiabatic or first-sound velocities, while high-frequency sound waves have zero-sound velocities, which are expected to be slightly higher. This effect depends on the temperature in two ways. The difference between zero and first sound, which approaches zero at 0 K, increases linearly with increasing temperature and, in addition, because of the temperature dependence of Γ, the transition region itself will be shifted towards higher frequencies at higher temperatures, and vice versa.

Zero- and first-sound elastic constants have been observed in solid krypton near its triple point using Brillouin and inelastic neutron scattering (Jackson *et al* 1973, Skalyo and Endoh 1973), the difference being as much as 12%. A different temperature dependence was found in KBr by Svensson and Buyers (1968), who compared ultrasonic and neutron data at 95 K and 463 K. In some favourable cases, it has been possible to perform ultrasonic measurements (Nava *et al* 1964, 1969, Blinick and Maris 1970) and Brillouin scattering experiments (Hasson and Many 1975) covering the transition region between zero and first sound. Blinick and Maris (1970) found a difference in the temperature dependence between high- and low-frequency sound in quartz of the order of 10^{-3}%.

The uncertainty in comparing zero- and first-sound elastic constants, which have been determined using different experimental techniques, arises from a lack of infor-

† Research supported by the Bundesministerium für Forschung und Technologie, W Germany.

mation on the transition region. Thus, it is often impossible to be certain that the condition for zero sound holds for all frequencies in inelastic neutron scattering experiments or that the Brillouin data really refer to the first-sound region. We therefore performed our inelastic neutron scattering experiments at four different temperatures and measured the dispersion of sound in a wavevector region $0{\cdot}06 \leqslant q/q_{\max} \leqslant 0{\cdot}25$. Our theoretical requirements were that we measure zero sound at room temperature and that our experiments cover the transition region at higher temperatures. The sample, a single crystal of NaF, 3 cm in diameter and 3 cm long with a [001] direction along the cylindrical axis, had a mosaic spread of less than 0·25°. Our measurements were performed at the High-Flux Reactor, Grenoble on the triple-axis spectrometer IN3, located at one of the neutron guide-tubes. We used an incident energy of 14·6 meV, produced by a (111) Bragg reflection from a copper monochromator and filtered by a pyrolytic graphite filter to remove higher orders. A germanium (111) crystal was used as an analyser.

Measurements at long wavelengths and small phonon energies usually require corrections:

(i) The variation of the neutron-scattering cross section across the energy spread of the observed neutron group results in a shift of the peak position towards lower energies.

(ii) Finite divergences—which can often be quite coarse in the vertical direction for ordinary triple-axis spectrometers—introduce an assymetry and shift the centre of the neutron groups.

All neutron groups have been corrected for effect (i). To keep the influence of the finite resolution as small as possible, we installed two Soller-type collimators between the sample furnace and the analyser crystal, which limited the horizontal and vertical divergence to 0·7°. For the incident beam, both divergences were 0·4°. Calculations showed that, for the particular phonon branches we intended to measure, shifts could be kept very small. In this letter, we present measurements with possible shifts less than the estimated errors. Experiments with different divergences showed this estimate to be reliable. We took extreme care to avoid systematic errors introduced by bad adjustment. At each temperature, the profiles of (200) and (220) reflections in wavevector space were measured and used to determine the adjustment of the spectrometer settings. The lattice constants derived from these measurements were in very good agreement with experimental data (Pathak *et al* 1963). Except for 700 K, the whole set of measurements was taken twice, in the heating-up process as well as cooling down. The temperature was kept at the desired value $\mp 5\,\%$.

While the majority of our measurements were made in the constant-$\boldsymbol{Q}$ mode of operation, a considerable number were repeated in the constant-E mode.

Figure 1 shows the results of our measurements at 295 K and 700 K for the two phonon branches we chose to investigate. Theoretically, the transverse acoustical branch in the $[\xi 00]$ direction should be the one with the smallest difference between zero- and first-sound velocities, while the greatest difference should be exhibited in the transverse acoustical branch in the $[\xi\xi 0]$ direction, with a velocity proportional to $(c_{11} - c_{12})^{1/2}$. A comparison with the ultrasonic data measured by Haussühl (1960) at 295 K and with those extrapolated to 700 K shows good agreement with these predictions. The estimated errors are smaller than the symbols used. While all points measured in the $[\xi\xi 0]$ direction at 295 K show a constant gradient, representing the zero-sound velocity, the non-linearity of the 700 K data indicates the transition region between zero and first sound.

Niklasson (1972) derives an expression for the elastic constants that describes the whole frequency region. In the limit $\Omega \gg \Gamma$, the results of ordinary perturbation theory

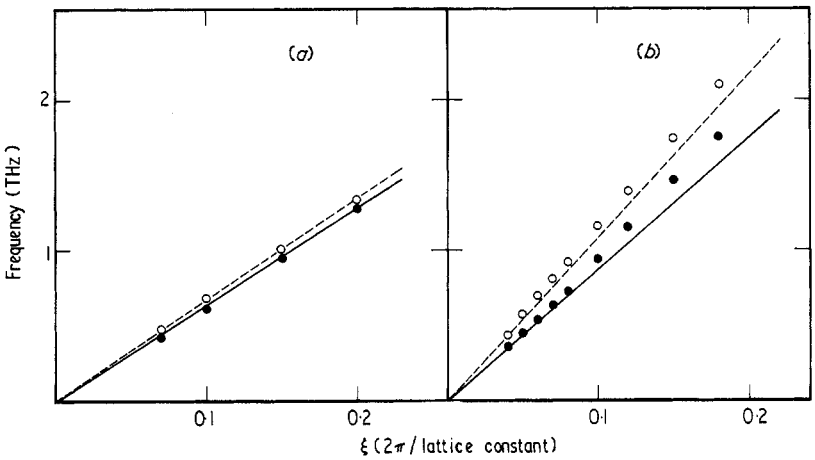

Figure 1. Phonon dispersion in (*a*) the $[\xi 00]$ TA and (*b*) the $[\xi\xi 0]$ T_2A transverse branches of sodium fluoride. The results of our measurements (○, 295 K; ● 700 K) are compared with Haussühl's (1960) extrapolated ultrasonic data at room temperature (– – – –) and at 700 K (———), assuming a linear temperature coefficient.

are obtained, while the limit $\Omega \to 0$ leads to first-sound elastic constants. We want to calculate the sound velocities of transverse modes, so we can therefore omit the difference between the adiabatic and isothermal elastic constants, because transverse isothermal sound equals transverse adiabatic sound. Assuming an averaged inverse lifetime Γ of the thermal phonons in the crystal, we obtain for the elastic constants in cubic crystals:

$$c_{\alpha\beta\gamma\delta}(T;\Omega\boldsymbol{Q}) = c^{\mathrm{is}}_{\alpha\beta\gamma\delta}(T) + \frac{\hbar^2}{k_B T}\frac{1}{NV}\sum_{qj}\gamma^{ij}_{\alpha\beta}(\boldsymbol{q})\gamma^{ij}_{\gamma\delta}(\boldsymbol{q})\omega^2(\boldsymbol{q}_j)$$
$$\times\, n(\boldsymbol{q}_j)\,[n(\boldsymbol{q}_j)+1]\left(\frac{\Omega}{\Omega - \boldsymbol{Q}\cdot\nabla_q\omega(\boldsymbol{q}_j) + 2\mathrm{i}\Gamma} + \frac{\Omega}{\Omega + \boldsymbol{Q}\cdot\nabla_q\omega(\boldsymbol{q}_j) + 2\mathrm{i}\Gamma}\right) \quad (1)$$

where $c^{\mathrm{is}}_{\alpha\beta\gamma\delta}(T)$ are the isothermal elastic constants and $\gamma^{ij}_{\alpha\beta}(\boldsymbol{q})$ the microscopic Grüneisen parameters. Our numerical calculations were based on a breathing shell model for the frequencies $\omega(\boldsymbol{q}_j)$ and eigenvectors of the modes and on realistic Grüneisen parameters (Jex 1974). Calculations were made to fit the third-order coupling constant to the experimental values of the thermal expansion and to the pressure dependence of the phonon frequencies.

To compare our experimental data with theory, we have calculated the frequency dependence of the sound velocity for the $[\xi 00]$ TA and the $[\xi\xi 0]$ T_2A branches, according to equation (1). We chose $c^{\mathrm{is}}_{\alpha\beta\gamma\delta}(T)$ and Γ as parameters. Obviously c^{is}_{44} and $\frac{1}{2}(c^{\mathrm{is}}_{11} - c^{\mathrm{is}}_{12})$ should coincide with ultrasonic data, while Γ should show a temperature dependence, according to lifetime calculations of thermal phonons.

Figure 2 shows the experimental data with our theoretical results. At room temperature, nearly all measured phonon frequencies belong to the zero-sound region, while at 500 K and 600 K there is a steep gradient, indicating that the measurements cover a large part of the transition region. At 700 K, the lowest frequencies are close to the first sound. The agreement between experiment and theory is quite satisfactory. Both the order of magnitude of the effect and the wavevector dependence of the sound velocity are well described.

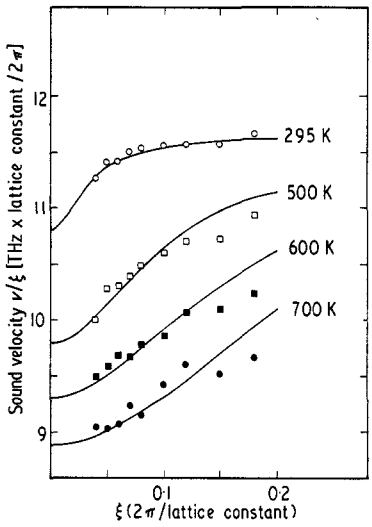

Figure 2. Sound velocity versus wavevector component ξ in the $[\xi\xi 0]$ T_2A branch at four temperatures. Experimental values (points) are compared with theoretical results (full curves).

Table 1 shows the values of Γ and $c^{is}_{\alpha\beta\gamma\delta}$. The order of magnitude as well as the temperature dependence of the averaged inverse lifetime seem reasonable. If we compare the isothermal elastic constants of our calculation with the ultrasonic data of Haussühl (1960)—which give $36{\cdot}4 \times 10^{10}$ dyn cm^{-2} at room temperature and, with the assumption that Haussühl's temperature coefficient remains constant over the whole temperature range, extrapolates to $23{\cdot}2 \times 10^{10}$ dyn cm^{-2} at 700 K—we find good agreement with our results. From our theoretical calculations for the transition between zero and first sound in the $[\xi 00]$ TA branch, we expected differences of 2% at the most in the sound velocity, even at 700 K. Since our experimental data scatter less than 3%, we take this as an indication for correct adjustment.

Table 1. Parameters for our numerical calculations: isothermal elastic constants and averaged inverse lifetimes of the thermal phonons in the crystal.

T (K)	$\frac{1}{2}(c^{is}_{11} - c^{is}_{12})$ (10^{10} dyn cm^{-2})	Γ (THz)
295	35·3	0·16
500	28·6	0·48
600	25·7	0·80
700	23·5	1·11

In table 2, room-temperature values of the elastic constants in the first-sound region are compared with zero-sound elastic constants from inelastic neutron scattering experiments. The data obtained from this work are derived from frequencies measured in the

Table2. Comparison of the ultrasonic data of Haussühl (1960) and the elastic constants derived from inelastic neutron scattering experiments at room temperature from both this work and from Buyers (1967). All values are in units of 10^{10} dyn cm^{-2}.

	Haussühl (1960)	This work	Buyers (1967)
$\frac{1}{2}(c_{11} - c_{12})$	36·4	40·5	42·5
c_{44}	28·1	27·5	29·8

region $q/q_{max} \geqslant 0{\cdot}1$ and the data from Buyers (1967) are the best fit values. In table 3, we compare the differences between the zero- and first-sound elastic constants with theoretical values.

Table 3. Differences between the zero- and first-sound elastic constants obtained by various workers at room temperature. Haussühl's (1960) ultrasonic values are subtracted from the values obtained from (*a*) this work, theory; (*b*) this work, experimental; and (*c*) Buyers (1967), best fit. All values are in units of 10^{10} dyn cm^{-2}.

	(*a*)	(*b*)	(*c*)
$\Delta\frac{c_{11} - c_{12}}{2}$	+5·3	+4·1	+6·1
Δc_{44}	+0·2	−0·6	+1·7

This investigation is the first attempt to study the transition region between zero and first sound by means of inelastic neutron scattering. For the first time, with this measurement, it is possible to determine the range of the transition region at different temperatures. The experimental data in the transition region are well described by the use of an averaged inverse lifetime. In conclusion, we want to note that we also found striking effects concerning the widths of the observed neutron groups. A weak frequency dependence at room temperature indicates the zero-sound regime, where the damping should be linear in the frequency, while a sharp increase at 700 K indicates the transition region or nearly first sound, where the damping is proportional to the square of the frequency.

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