Phonon Anomalies in Nb_3Sn

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Small single crystals of Nb_3Sn were grown and used to study the lattice dynamics by means of inelastic neutron scattering. Almost complete sets of phonon dispersion curves could be obtained for the main symmetry directions. The results are generally in very good agreement with the predictions of Weber based on the nonorthogonal-tight-binding method. In particular it has been confirmed that the (111) LA branch exhibits a pronounced anomaly.

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In spite of intensive investigations which have been carried out on A_3B compounds with the $A15$ structure, the question has remained open why a number of them show very high superconducting transition temperatures T_c. Likewise the origin of the cubic-to-tetragonal phase transition, so far observed for stoichiometric NB_3Sn and V_3Si, and its relation to the occurrence of high-T_c values, is still a matter of debate. Recently Weber[1,2] has presented calculations of the phonon dispersion curves and the electron-phonon coupling in Nb_3Sn based on the nonorthogonal-tight-binding method[3] and using realistic energy bands.[4] His main result was that the feature of linear A-atom chains in the $A15$ structure is of great importance for the strong electron-phonon coupling and thus for the high-T_c values. Only those phonon modes interact strongly with the electrons near the Fermi energy E_F, where Nb atoms move opposite to their neighbors within one chain. The frequencies of these phonons are drastically lowered compared to those of the low-T_c reference compound Nb_3Sb and exhibit anomalous dispersion, especially along the [111] direction. At the time of the publication of Weber's results there were hardly any experimental data on the lattice dynamical properties of Nb_3Sn available to allow a detailed comparison. Recently, a neutron scattering study of [111] LA phonons has been carried out by Axe and Shirane,[5] aiming at a check of one of the most spectacular predictions of Weber, i.e., the occurrence of a pronounced anomaly in the [111] LA branch at $\approx (0.25, 0.25, 0.25)$. They were able to determine the dispersion of (ζ, ζ, ζ) LA phonons up to $\zeta \leq 0.24$. In this range of ζ values no indication of the predicted anomaly was found.

In this Letter we report on a complete study of all the 24 branches of the Nb_3Sn phonon-dispersion curves. Our results agree in general very well with Weber's predictions and confirm the occurrence of a pronounced anomaly in the [111] LA branch.

Recently we were able to grow small Nb_3Sn single crystals of excellent quality.[6] A chemical analysis revealed that their composition is very close to the stoichiometric one. This was confirmed by measurements of T_c and the tetragonal transformation temperature T_M ($T_c = 18.0 \pm 0.1$ K, $T_M = 35$–50 K). By combining four of these crystals on the same holder we arrived at a specimen with a total volume of 0.05 cm^3 and an effective mosaic spread of less than 0.2°. We note, that the total volume is not larger than that of the crystal used in the previous inelastic neutron scattering studies by Shirane and Axe. Moreover, our experiments were performed not at a high-flux reactor, but at the medium-flux reactor at Saclay. Yet an adaption of the neutron spectrometer to the investigation of very small samples enabled us to measure most of the optic branches in the main symmetry directions, including the highest modes: a vertically curved Cu(111) crystal and a horizontally curved pyrolytic graphite (002) crystal were chosen as monochromator and analyzer, respectively. The commonly used Soller collimators were replaced by slits, which yielded an effective collimation α_0, α_1, α_2, α_3 of 60′, 30′, 60′, 60′, respectively. For several scans, α_2 was increased from 60′ to 120′, which did not affect the energy resolution. An example of a scan for an optic phonon with large inelastic structure factor is given in Fig. 1, which shows that, in spite of the small sample volume, the

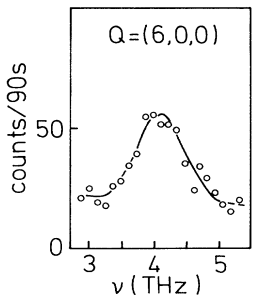

FIG. 1. Example of an inelastic neutron-scattering peak for an optical phonon with a relatively large inelastic structure factor (Γ_{15} mode). The sample volume was 0.05 cm^3.

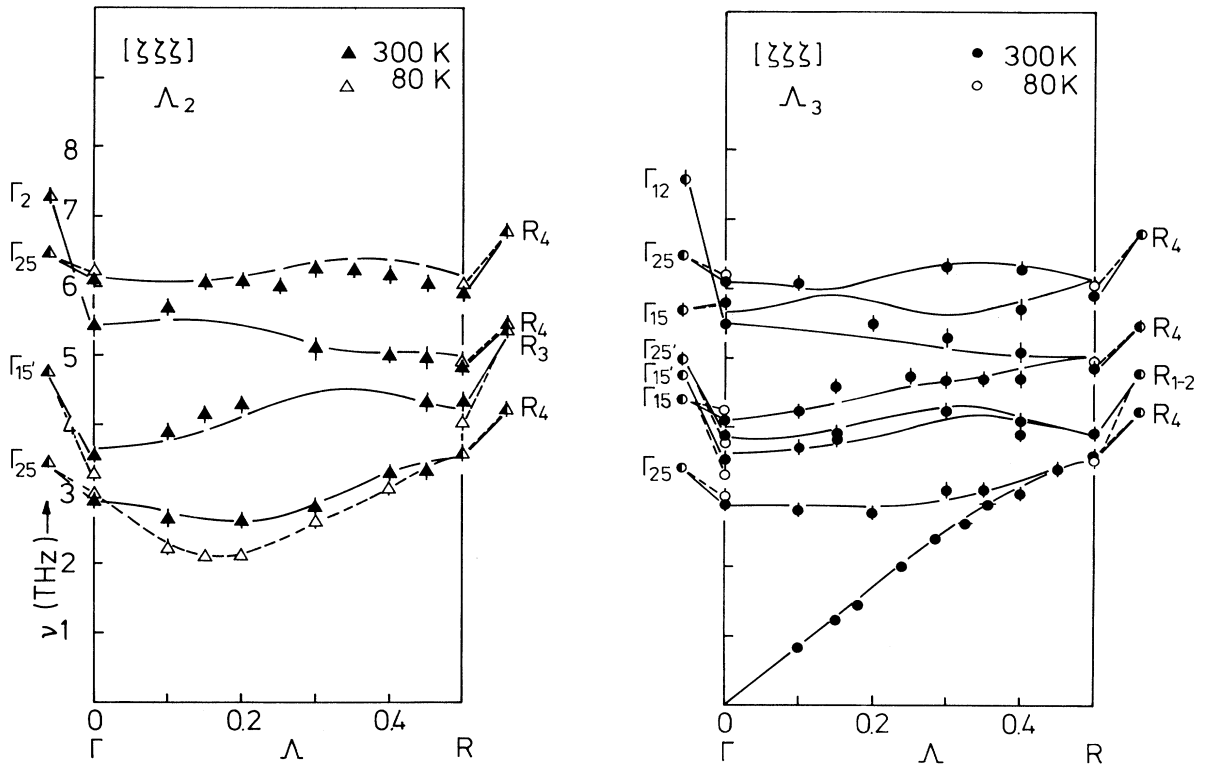

FIG. 2. Phonon dispersion curves in Nb_3Sn at room temperature in the [111] direction. Data are shown for the Λ_2 and Λ_3 representations on the left-hand side and on the right-hand side, respectively (data for the Λ_1 representation are given in Fig. 3). Full lines are calculated from a 34-parameter Born–von Kármán model. Open symbols and the broken line denote additional data taken at 80 K. The symbols outside the diagrams depict data for the low-T_c reference compound Nb_3Sb (after Ref. 8) and connect by full and dashed lines to the corresponding modes in Nb_3Sn.

counting rates were quite satisfactory.

Most of the measurements were performed at room temperature. Selected phonons were also investigated at 80 K on the conventional triple-axis spectrometer IN8 in Grenoble.

The room-temperature experiments yielded a fairly complete set of disperision curves for the main symmetry directions. The most informative results are those for the [111] direction which are plotted in Figs. 2 and 3. The data for the [100] and [110] directions will be given in a subsequent publication.[7]

The lines in Fig. 2 are the result of a fit based on a 34-parameter Born–von Kármán model including general forces between atom pairs within a maximum distance of 1.5 lattice constants. The need for such a complicated model was to assign as reliably as possible the measured phonon groups to the many different branches. In spite of the very large number of disposable parameters the agreement between calculated and experimental frequencies and especially between calculated and experimental intensities is still not perfect. We note that for the low-T_c $A15$-compound Nb_3Sb a similar quality fit can be obtained with a much simpler model, i.e., a six-parameter Born–von Kàrmàn model with a range of the forces of not more than 0.61 lattice constants.[8]

The rather long range of the forces indicates the presence of strong electron-phonon coupling effects, as had to be expected for this high-T_c superconductor. Strong-coupling phonon modes can be identified by comparison of the Nb_3Sb dispersion curves to those of the low-T_c reference compound Nb_3Sb (Ref. 8) and also by a study of the temperature dependence of the phonon frequencies. In this way a detailed check of Weber's theory mentioned above is possible: Compared to Nb_3Sb, the frequencies in Nb_3Sn are generally softer by about 10%. The overall softening has already been known from measurements of the phonon density of states on polycrystalline samples[9] and is correctly reproduced by the theory. A closer look reveals that some specific modes are lowered much more than 10%. According to Weber only those phonon modes should couple strongly to the electronic system, where neighboring Nb atoms of one chain move opposite to each other, either along or perpendicular to the chains. The strong coupling of these modes is a direct consequence of the specific orbital character of the flat energy bands near E_F: These bands are made up almost

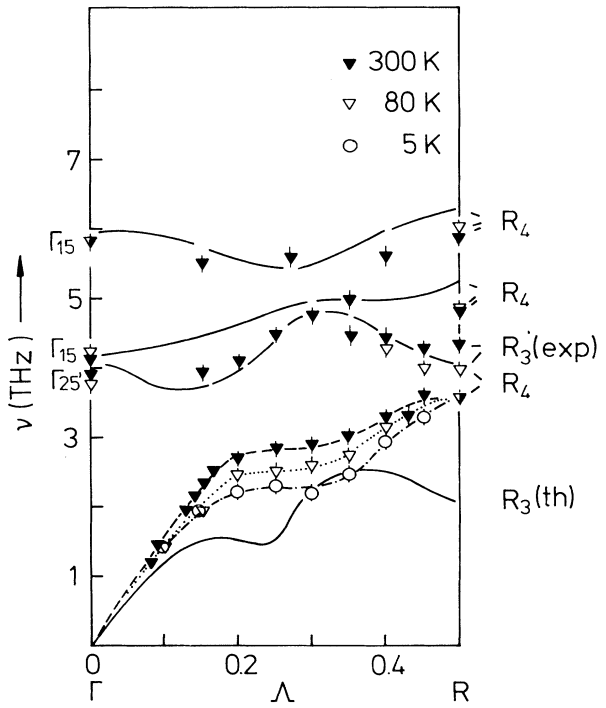

FIG. 3. Phonon disperison curves in Nb_3Sn for the Λ_1 representation at three different temperatures (5-K data after Ref. 7). Full lines have been calculated from a microscopic theory by Weber (Refs. 1 and 2) prior to the measurements. Dashed, dotted, and dot-dashed lines are guides to the eye only.

exclusively from Nb orbitals extending along the chains.[4] As a consequence, any relative motions of neighbor chain atoms cause big changes of the overlap of these orbitals and thus a strong electron-phonon coupling. On the other hand, a vibration of the Nb atoms against the Sn sublattice should lead to a weak electron-phonon coupling, as there is hardly any admixture of Sn electronic states to the bands near E_F.[4]

The distinction between modes for which a strong or a weak coupling is expected, can be made most easily for the Γ point. The Γ_{15} and Γ_{25} modes should have weak coupling, because here the chain atoms move in phase against other chains and/or the Sn sublattice. On the other hand, the Γ_{12} and Γ_2 modes (longitudinal intrachain vibrations) as well as the $\Gamma_{25'}$ and $\Gamma_{15'}$ modes (transverse intrachain vibrations) should exhibit strong coupling. A similar, but less clear-cut distinction can be given for the R point: Here the R_3 and $R_{1\text{-}2}$ modes should have much stronger coupling than the R_4 modes. Indeed, we find that just those Γ- and R-point modes, which should couple strongly to the electronic system, are much more depressed in Nb_3Sn compared to Nb_3Sb than the others (see Fig. 2). Moreover, just these modes soften upon cooling from 295 to 80 K, whereas the other ones remain stable or even show a slight hardening.

The most dramatic of the anomalous features in the phonon dispersion curves predicted by Weber is a pronounced dip in the (111) LA branch at about (0.25, 0.25, 0.25). As mentioned above, Axe and Shirane recently have performed measurements designed to explore the correctness of this predicted feature.[5] The conclusions of that study were based on data for $(\zeta\zeta\zeta)$ LA phonons with $\zeta \leq 0.24$ at $T = 275$ K and $\zeta \leq 0.15$ at low temperatures, the authors being unable to observe $(\zeta\zeta\zeta)$ LA phonons for larger ζ values. Within the accessible ζ range there was no indication of an anomaly around $\zeta \approx 0.25$, in contrast to the predicted shape of the LA branch. Therefore it is reasonable that Axe and Shirane reported that the predicted anomaly was not observed.

In our first attempts to measure the $(\zeta\zeta\zeta)$ LA phonons we reproduced the data given in Ref. 5, but lost the intensity at the same ζ value as did Axe and Shirane, i.e., $\zeta = 0.24$. Progress was achieved only after the determination of many optic phonons, which allowed us to refine our lattice dynamics and thus enabled us to know in which Brillouin zones the remaining part of this branch had to be measured. It turned out that there is an anomaly in the (111) LA branch, but less pronounced than expected and somewhat shifted in position to $\zeta \approx 0.3$ (see Fig. 3). Upon cooling a frequency decrease up to 20% has been observed for phonons in this region, which confirms the view that these phonons are anomalous, and brings the size of the anomaly much nearer to the predicted one. We think that this result adds credence to Weber's calculations, although the agreement between theory and experiment is not quantitative.

As can be seen from Fig. 3, the agreement between prediction and observation is less satisfactory for the R_3 frequency. This mode is indeed considerably lowered when compared to the same mode in Nb_3Sb, but the theory overshoots this effect by far. On the other hand, the frequencies of the upper three Λ_1 branches agree nicely with the calculated values.

The local minimum in the (111) LA branch resembles closely the phonon anomalies found in other high T_c materials like Nb or the refractory compounds.[10-12] Another, somewhat shallower anomaly has been observed in the lowest Λ_2 branch halfway to the zone boundary. Temperature-dependent measurements have confirmed the anomalous nature of this region, showing a strong phonon softening upon cooling for ζ values around $\zeta = 0.2$, i.e., up to 25%. Again, this anomaly has been predicted by Weber's theory.

As the anomalies in the Λ_1 and Λ_2 branches are reminiscent of those in other high-T_c superconductors, one may suppose that their position is linked to nesting features of the Fermi surface. However, the theoretical analysis of Weber[13] does not confirm this

idea. Instead, we have found that changes of the phonon eigenvectors play an important role: A polarization analysis revealed that the frequency minima are correlated with large transverse vibration amplitudes of the Nb atoms against their nearest neighbors within the chains. This observation confirms the picture given above that strong electron-phonon coupling is expected only for modes where neighboring atoms of one chain move opposite to each other.

In conclusion, an inelastic neutron-scattering study of the high T_c superconductor Nb_3Sn revealed several anomalous features in the phonon dispersion curves, which agree well with those predicted by a recent theoretical investigation.

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