

Comparative investigation of temperature-induced phonon-frequency shifts in CeSn_3 and LaSn_3

O. Blaschko, G. Krexner, and P. Weinzierl

Institut für Experimentalphysik der Universität Wien, Strudlhofgasse 4, A-1090 Wien, Austria

W. Assmus

Physikalisches Institut der Universität Frankfurt, Robert-Mayer-Strasse 2-4, D-6000 Frankfurt, Federal Republic of Germany

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Phonon frequencies of longitudinal- and transverse-acoustic modes have been determined in the mixed-valence compound CeSn_3 at 295 and 10 K. For comparison, temperature-induced phonon-frequency shifts were also measured in the integral-valence isostructural compound LaSn_3 . No evidence has been found that the mixed valence significantly alters the lattice dynamics of CeSn_3 as a function of temperature. The difference between the thermal expansion coefficients of CeSn_3 and LaSn_3 below room temperature is in agreement with differences in the respective mode Grüneisen parameters of the two substances.

INTRODUCTION

Certain rare-earth compounds exhibit anomalous properties in a number of physical quantities such as the thermal expansion, magnetic susceptibility, or lattice constants (deviation from Végard's law). This anomalous behavior has been related to a peculiar electronic structure arising from the presence of $4f$ states in the vicinity of the Fermi level, thus leading to a mixed-valence state of the rare-earth ion.^{1,2} Experimentally, it was found that investigations of the intermediate rare-earth valences based on anomalies in macroscopic bulk properties generally yield higher values in contrast to results obtained from methods exploring the electronic structure more directly (e.g., L_{III} absorption spectroscopy³). Furthermore, it is still an open question if the ionic promotional model for $4f^n \rightarrow 4f^{n-1}$ electronic transitions applies or whether a band picture with hybridization between the f and sd bands is more adequate.

So far, anomalous properties due to mixed valence have been extensively investigated mainly in two groups of materials: samarium compounds with NaCl structure and cerium alloys whose crystal lattice belongs to the Cu_3Au type. Investigations of the lattice dynamics of mixed-valence systems were guided by the search for phonon anomalies induced by the fluctuating valence of the rare-earth ion. In compounds with NaCl structure, i.e., SmS and $\text{Sm}_{1-x}\text{Y}_x\text{S}$, which show a semiconductor-metal phase transition with pressure and temperature, respectively, strong anomalies have been found in the longitudinal-acoustic (LA) phonon branches.⁴ These anomalies could be described within the framework of a breathing-shell model where the breathing deformability was taken to reflect the changing nonintegral valence.⁵

On the other hand, in cerium compounds with the Cu_3Au structure like CeSn_3 , the phonon dispersion curves do not exhibit any conspicuous features but are similar to those of isostructural systems like LaSn_3 where the rare-earth ion is in a well-defined $3+$ -valence state. Therefore, the lattice dynamics of both systems

appears to be rather similar although the two compounds differ markedly in a number of microscopic and macroscopic properties.^{6,7}

Calculations of phonon frequencies in CeSn_3 and CePd_3 indicated that an interaction between localized $4f$ electrons and phonons would affect mainly the longitudinal-acoustic branches in the range $q \leq 0.3$. Contrary to the situation in compounds with the NaCl structure, in the present case anomalies should be found in all principal symmetry directions ([100], [110], [111]). Moreover, it was conjectured that phonon softening might occur upon application of pressure.⁸

A recent neutron scattering investigation of the pressure-induced phonon-frequency shifts in CeSn_3 up to 4 kbar, however, did not reveal any drastic pressure effects.⁹ The determination of mode Grüneisen parameters (mode γ 's) for several transverse and longitudinal phonons in the [100] and [110] directions generally yielded normal positive values. Yet, two findings should be noted: First, the LO_1 [100] phonon at the zone center exhibits an unusually high positive Grüneisen parameter $\gamma \sim 5$. Secondly, in the low- q region the mode γ 's of the LA branches are lower than those obtained for the respective transverse branches by a factor of ~ 1.5 .

This latter result is unexpected in the following respect: Presently, mode Grüneisen parameters for substances directly comparable to CeSn_3 are not available. However, values for the pressure dependence of the elastic constants obtained from ultrasonic measurements in the long-wavelength limit yield a good estimate of the mode γ 's as long as the acoustic dispersion curves can be regarded as linear. A survey of the available data for alloys with Cu_3Au structure shows that the mode Grüneisen parameters based on the above extrapolation generally are higher for the longitudinal than for the transverse branches.¹⁰ Even within the large number of cubic alloys or elements whose structure is different from Cu_3Au only very few cases can be found where the mode γ 's of the LA branches are slightly lower than for the transverse phonons. So, CeSn_3 is unique in that the

TA-mode Grüneisen parameters in the low- q region where the linear approximation is still valid are significantly larger than the values obtained for the LA modes.

In the present paper we continue the search for possible lattice-dynamical effects in CeSn_3 due to mixed valence by investigating the temperature dependence of the phonon dispersion. Mixed valence entails “anomalous” behavior in various properties (magnetic susceptibility, resistivity, thermal expansion) mostly observed as a function of temperature between room temperature and absolute zero. In addition, the change in the specific volume of CeSn_3 between 300 and 0 K is more than twice as large as the volume reduction brought about by a pressure of 4 kbar which was applied in the previous investigation.⁹ In the present work, frequency shifts with temperature are measured in CeSn_3 and for comparison in the isostructural compound LaSn_3 where the rare-earth ion is assumed to be in an integral-valence $3+$ state.

EXPERIMENT

The phonon measurements were performed on two spectrometers at the Orphée reactor at Saclay. The experiment on CeSn_3 was done on the thermal-neutron triple-axis spectrometer T2 whereas LaSn_3 was investigated on the triple-axis spectrometer VALSE located at a cold-neutron guide position.

Two single crystals of CeSn_3 and LaSn_3 with a mosaic spread of 1.5° and 3° , respectively, were used as samples. The LaSn_3 sample was the best of several crystals which had been grown. The crystals were mounted in a closed-cycle cryostat with a $[100]$ direction perpendicular to the scattering plane.

The large mosaic spread of the LaSn_3 crystal engendered an additional line broadening, impairing especially low- q transverse-acoustic phonons whose frequency shifts, therefore, could not be evaluated. Phonons were investigated in CeSn_3 and LaSn_3 first at room temperature and subsequently at 10 and 20 K, respectively. The peak positions were determined by Gaussian fits to the measured phonon intensities, the difference in position yielding the phonon-frequency shift as a function of temperature.

RESULTS

The relative phonon-frequency shifts as a function of temperature were evaluated in terms of

$$\gamma = -(\Delta\omega/\omega)/(\Delta V/V), \quad (1)$$

as described in Ref. 11, thus facilitating the comparison with the results of the previous investigation⁹ of pressure-induced frequency shifts ($\Delta V/V$ denotes the relative volume change with temperature).

(a) CeSn_3 : Figure 1 gives the results of the present experiment [Fig. 1(a)] together with the mode Grüneisen parameters obtained previously [Fig. 1(b)]. Comparison shows that the values of the temperature-induced frequency shifts essentially confirm the earlier results ob-

tained on application of pressure: The frequency shifts of the LA phonons in the lower- q region are smaller than those found for the transverse modes. The optic phonon at the zone center again shows a rather high relative frequency shift.

(b) LaSn_3 : The results for some longitudinal- and transverse-acoustic phonons are shown in Fig. 2. Due to the large mosaic spread of the crystal the quality of the data is less satisfactory than for CeSn_3 . The frequency shifts with temperature obtained for the LA $[110]$ branch are similar to those in CeSn_3 . The shifts in the LA $[100]$ direction are centered around zero. Surprisingly, the TA modes behave in an unexpected way. The phonons near the zone boundary ($q=0.4$ and 0.5) exhibit a significant softening of a few percent upon decrease of temperature to 20 K. The TA $[100]$ phonon at $q=0.3$ is the only one to show a positive frequency shift resembling that obtained in CeSn_3 .

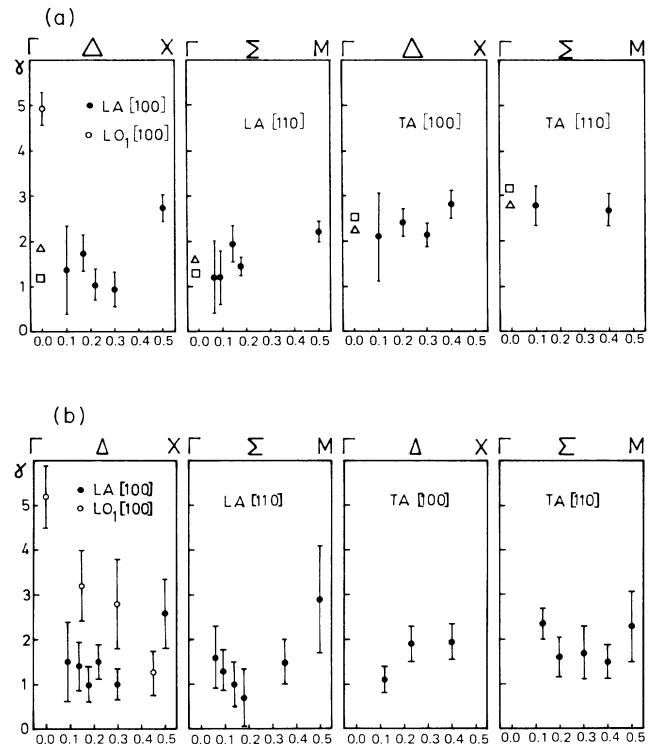


FIG. 1. (a) Relative phonon-frequency shifts in CeSn_3 as a function of the reduced wave vector q determined by measurements at room temperature and 10 K. Data are presented as thermal mode Grüneisen parameters $\gamma = -(\Delta\omega/\omega)/(\Delta V/V)$ with $(\Delta V/V) = -0.0192$. The higher values obtained for the longitudinal branches at $q=0.5$ probably are due to the exchange of eigenvectors between the optic and acoustic branches [cf. Fig. 1(b)]. Estimates of the frequency changes at $q=0$ were derived from measurements of the temperature dependence of the elastic constants between 0 and 250 K (Ref. 15, \square) and between 0 and 300 K (Ref. 17, \triangle). (b) Microscopic Grüneisen parameters in CeSn_3 derived from measurements at 0 and 4 kbar. $\Delta V/V = -0.0075$ (Ref. 9).

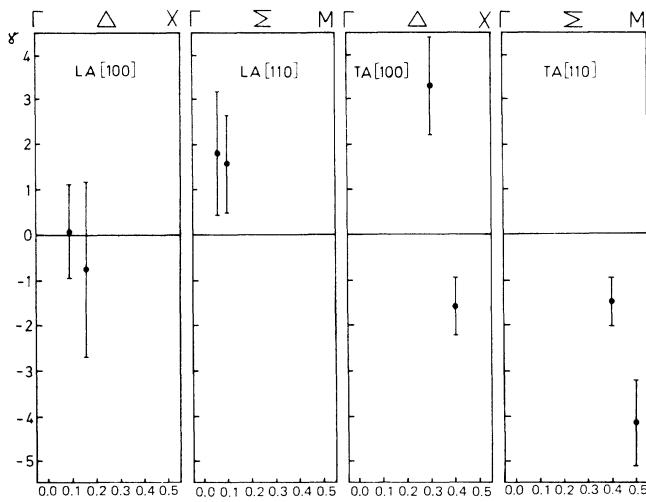


FIG. 2. Relative phonon-frequency shifts in LaSn_3 derived from measurements at room temperature and at 20 K. As in Fig. 1(a) results are presented as thermal mode γ 's with $\Delta V/V = -0.0088$. Due to the large mosaic spread of the sample only few values could be determined.

DISCUSSION

Comparison of the changes of the phonon frequencies in CeSn_3 with temperature and with pressure shows that the mode Grüneisen parameter dispersions derived from the respective temperature and pressure variation are on the whole very similar. The values coincide within the error bars for the longitudinal branches. For the transverse phonons the thermally induced frequency shifts appear to be slightly larger.

The search for possible differences of the temperature-induced frequency shifts occurring between CeSn_3 and LaSn_3 can be summarized as follows.

(i) If the frequency variations with temperature are normalized to the same relative volume change, both CeSn_3 and LaSn_3 exhibit small frequency shifts for the low- q region of the LA branches. The shift of the LA[100] phonons in LaSn_3 is even slightly smaller than in CeSn_3 . Therefore, the low values of the LA mode γ 's in CeSn_3 cannot be regarded as a mixed-valence phenomenon.

(ii) The frequencies of the TA phonons in CeSn_3 increase upon cooling to 10 K as expected for a standard anharmonic solid. In contrast to this, the TA phonons in LaSn_3 become softer near the zone boundary when the temperature is reduced. This finding, seemingly rendering LaSn_3 more "anomalous" than CeSn_3 , is related to results of an investigation of the temperature dependence of phonons in LaSn_3 between 750 and 295 K performed by Stassis and co-workers.¹² Their experiment yielded a frequency decrease of optic phonons near the center of the Brillouin zone with decreasing temperature while the TA-phonon energies for $q \leq 0.2$ still exhibit a slight increase between 750 K and room temperature.

The present results therefore indicate that at low temperatures the phonon softening extends to further parts of the Brillouin zone, thus involving a considerable portion of the phonon density of states. This behavior probably being due to the electron-phonon interaction should be discussed with regard to the high superconducting transition temperature of LaSn_3 ($T_c = 6.42$ K).

(iii) Finally, from a lattice-dynamical point of view, the present investigation may help to explain the difference in the thermal expansion coefficients of CeSn_3 and LaSn_3 in the range between room temperature and 10 K. Above ambient temperature the thermal expansion coefficients of the two substances are relatively close to each other. However, this is no longer the case below room temperature because of the well-known anomalous maximum of the thermal expansion coefficient occurring in CeSn_3 near 130 K.^{7,13-15} The ratio of the average thermal expansion coefficient $\bar{\alpha}(T)$ between room temperature and 10 K (20 K) obtained from the lattice-parameter data of the present investigation is $\bar{\alpha}(\text{CeSn}_3)/\bar{\alpha}(\text{LaSn}_3) = 2.2$, where the high value of the thermal expansion coefficient of CeSn_3 is supposed to be due to a concomitant change of the cerium valence approaching the $3+$ state with increasing temperature.

The linear thermal expansion coefficient $\alpha(T)$ is related to the microscopic Grüneisen parameters as obtained by varying the pressure at constant temperature via

$$\alpha(T) = \frac{k_B}{3B_T V} \sum_{\mathbf{q}, j} \gamma(\mathbf{q}, j) c(\mathbf{q}, j; T), \quad (2)$$

where k_B denotes Boltzmann's constant, V the volume of the sample, B_T the isothermal bulk modulus, and $c(\mathbf{q}, j; T)$ the Einstein specific-heat function (\mathbf{q} is the reduced wave vector and j the branch index).

Insertion of the respective quantities for CeSn_3 and LaSn_3 yields the following result: V differs by about 3% between the two substances. Existing measurements for B_T give a higher value for LaSn_3 but are somewhat contradictory (cf. Refs. 9, 14, and 15). However, a rough estimate can be derived from the linear sections of the phonon dispersion curves¹⁶ by using the relation $B_T = \frac{1}{3}(c_{11} + 2c_{12})$. For low q the dispersion curves of CeSn_3 and LaSn_3 practically coincide and it is a safe upper limit to assume that $B_T(\text{LaSn}_3)$ will not exceed $B_T(\text{CeSn}_3)$ by more than 20%. This is partly compensated by the fact that the phonon energies of CeSn_3 are on the average slightly higher than those of LaSn_3 , thus lowering the corresponding values of the Einstein weighting function. Therefore, the difference in the thermal expansion coefficients of CeSn_3 and LaSn_3 has to be ascribed for the most part to different behavior of the respective mode γ 's.

Presently mode γ 's are only available for CeSn_3 .⁹ Yet in many cases frequency shifts determined by varying the temperature at constant pressure yield a good approximation to the microscopic Grüneisen parameters. For example, this is well justified for CeSn_3 , as can be seen by comparing Figs. 1(a) and 1(b). On the assumption that this also holds true for LaSn_3 , the mode γ 's in (2) can be replaced to first order by the respective

thermal frequency shifts [cf. Figs. 1(a) and 2]. Comparison shows that the normalized frequency shifts in LaSn_3 are smaller than in CeSn_3 within the low- q region of the LA[100] phonons and become negative for the TA branches near the zone boundary. Insertion in (2), consequently, leads to a result which is in qualitative agreement with the difference of the thermal expansion coefficients observed in CeSn_3 and LaSn_3 .

Considering the present investigation together with earlier results⁹ one can conclude that neither the pressure nor the temperature-induced phonon-frequency shifts in CeSn_3 provide evidence for any coupling of the mixed-valence state of the cerium ions to lattice vibrations in the [100] or [110] directions. Likewise this

should apply to the [111] direction, since in compounds with Cu_3Au structure all principal symmetry directions should be affected in a similar way. However, there are some features of the thermal-mode γ 's in the isostructural compound LaSn_3 serving as reference which are not fully understood at present. In order to get a more complete picture complementary measurements on LaSn_3 would be useful.

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