Phonon dispersion in intermediate-valence $Sm_{0.75}Y_{0.25}S$

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Phonon dispersion has been measured in an intermediate-valence-state system. The phonons of intermediate valence $Sm_{0.75}Y_{0.25}S$ are vastly different from those of the SmS and YS constituents. The LA phonons are unusually soft compared to the TA and have anomalous width, particularly for the [111] direction. The LO phonons lie below the TO. Temperature-dependent measurements show that the anomalous phonon properties change with changing valence.

Valence instabilities and fluctuations in rare-earth materials have been the subject of intense experimental and theoretical research.[1,2] Anderson[3] has given an excellent assessment of the current understanding of valence instabilities, including the importance of the phonon dispersion in an intermediate-valence-state system. It is found that the phonon dispersion of $Sm_{0.75}Y_{0.25}S$ is strongly modified by the valence instability. We conclude that in this case the electronic configurations and the phonons form a strongly coupled system.

SmS was shown to be an unstable valence material by Jayaraman *et al.*[4] who suggested that the pressure-induced semiconductor to metal transition found at 6.5 kbar was associated with the conversion of Sm^{2+} to Sm^{3+}. The unusual magnetic properties associated with this lattice collapse led Maple and Wohlleben[5] to the conclusion that in the collapsed phase both Sm^{2+} and Sm^{3+} coexist in a fluctuating-valence state as described in Hirst.[6] This case, in which all Sm sites are equivalent and the average valence is nonintegral, is called the homogeneous intermediate-valence state.[2]

When SmS is alloyed with 15-at.% YS a similar lattice collapse occurs and the intermediate-valence state of Sm can be studied without the use of high-pressure cells.[7] X-ray photoemission,[8,9] Mössbauer isomer shift,[10] and magnetic measurements[11] have confirmed that $Sm_{1-x}Y_xS$ solid solutions ($x>0.15$) are intermediate-valence materials and show that the lattice parameter is a function of the electronic configuration. Sound velocity measurements by Melcher *et al.*[12,13] have shown that the room-temperature bulk modulus is soft in the intermediate-valence state, particularly near the valence transition ($x \gtrsim 0.15$).

Phonon dispersion measurements were made on triple-axis neutron spectrometers located at the High Flux Isotope Reactor. The measurements were made on a sample crystal grown from the melt by a method described previously.[14] The sample used was isotopically pure ^{154}Sm to avoid the large absorption cross section of naturally occurring Sm isotopes. The crystal of $Sm_{0.75}Y_{0.25}S$ used in our experiments is a gold color at room temperature with a lattice constant of 5.695 Å. As the temperature is lowered to 100 K the lattice constant increases smoothly to 5.760 Å and the color changes to purple. The transition is centered at about 200 K (5.725 Å) and extends over a temperature range of about 75 K. If we assume Vegards law, the lattice-constant measurements suggest that the configuration is 30-at.% Sm^{2+} at 293 K, 50-at.% Sm^{2+} at 200 K, and 70-at.% Sm^{2+} at 100 K.

The most striking attributes of the phonon measurements (Fig. 1) are given below. First, the longitudinal branches are soft compared to the transverse. This result is most striking for the [111] direction where the LA branch lies below the TA throughout most of the Brillouin zone. The LO branches are also unusually soft, lying below the TO branches, nearly everywhere. Second, the longitudinal phonons have anomalously broad widths, demonstrating strong coupling to the valence fluctuations. Third, the acoustic phonons are qualitatively different from those of the SmS and YS constituents.[15,16]

The LA and TA modes provide an interesting comparison. In all other known materials the LA phonons are more energetic than the TA near the zone center, contrary to the situation here. The slopes of our phonon branches near the zone center are in good quantitative agreement with the ultrasonic sound velocities.[12] Specifically, the [110] ultrasonic velocities, measured on a similar sample, were 2.29×10^5, 3.39×10^5, and 3.89×10^5 cm/sec for TA_1, LA, and TA_2; while

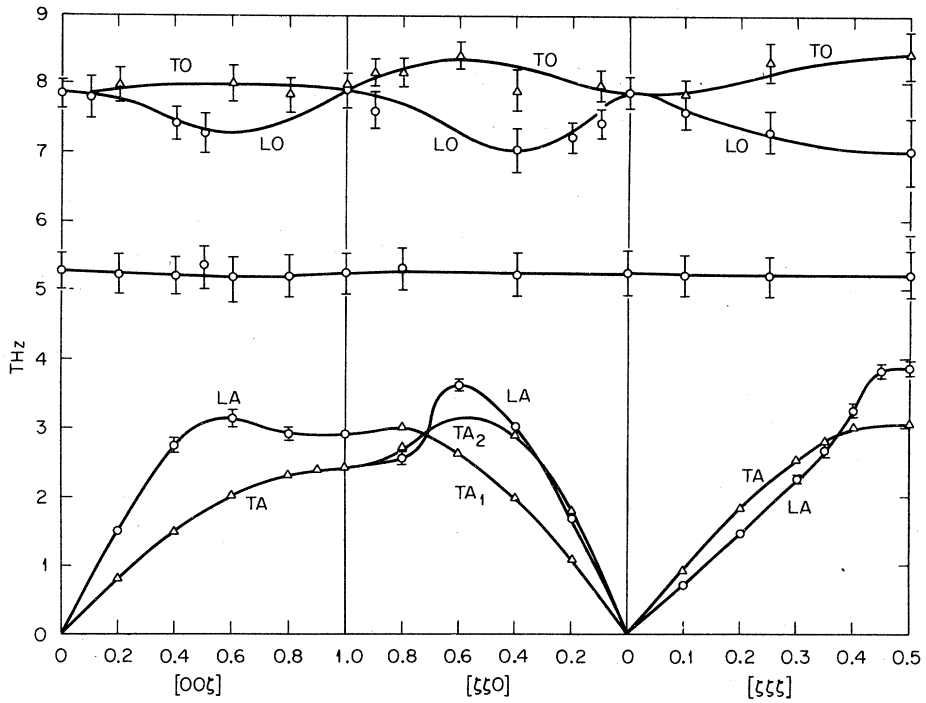

FIG. 1. Phonon dispersion curves for $Sm_{0.75}Y_{0.25}S$ measured at room temperature. The flat mode near 5 THz is the Y local mode.

from the neutron measurements we obtain $(2.21 \pm 0.04) \times 10^5$, $(3.3 \pm 0.1) \times 10^5$, and $(3.6 \pm 0.15) \times 10^5$ cm/sec. The new results (Fig. 1) show that the anomalous behavior is not restricted to the zone center but that all the longitudinal phonons are modified by the valence fluctuation, the effects being strongest in the [111] direction.

The longitudinal phonons are broad in energy particularly in the [111] direction. The [111] LA phonons are broadest (1.2 THz) near the region of largest softening, at about $\frac{2}{3}$ of the zone boundary, and become narrow at the zone center and zone boundary. The error bars shown in Fig. 1 indicate uncertainty in the phonon-peak positions. The transverse modes are found to be sharp in energy and their dispersion is normal in appearance. In regions where the transverse modes could be well focused, such as about 20% of the distance to the zone boundary in the [110] direction, widths as narrow as 0.10 THz were found. This result shows that the sample is of high quality and that the transverse modes are not strongly damped by the valence instability. The Bragg peaks of the crystal were also very sharp at room temperature indicating a high degree of uniformity of the crystal.

Contrary to most materials, the LO phonons in $Sm_{0.75}Y_{0.25}S$ and in YS lie below the TO phonons.[16] Measurements of the optical phonons were, however difficult because of the limited sample size (0.2 cm^3) and the small nuclear scattering cross section of sulphur. Furthermore, the LO phonons were quite broad (~2 THz) particularly at the [111] zone boundary where the LO mode extends downward to low energies. The optical-phonon energies thus have rather larger error bars associated with them than the acoustical modes which gave good neutron scattering intensity. The optical-phonon measurements were made at large-momentum transfers, where the magnetic form factor is very small, in order to avoid interference from the Sm^{2+} $J=0$ to $J=1$ magnetic transition, which lies at about 9 THz. Optical measurements[17] and results of x-ray diffraction determined Debye-Waller factors[18] have suggested that the LO phonon energy at the [111] zone boundary may be lowered at the transition, in agreement with our measurements.

Phonons play an important role in the intermediate-valence state because the $Sm^{3+}(f^5d)$ and $Sm^{2+}(f^6)$ electronic configurations are strongly coupled to the lattice.[19] This coupling occurs because the 3+ ionic radius is much smaller than the 2+ and because the d electron is sensitive to the crystal field. The Sm^{2+} and Sm^{3+} configurations are, therefore, associated with different unit-cell volumes. Consequently, the phonon modes which change the unit-cell volume will be most strongly affected by the valence instability. The TA modes, which to first order do not change the unit-cell

volume, should be less strongly affected than the longitudinal modes, which directly vary the distance between the atoms. These simple arguments are consistent with our results. The effect of the phase transition on the phonons is somewhat different than the usual soft-mode case, since by symmetry no single phonon corresponds to the combination of elastic constants that give the bulk modulus.[12,13,20] Thus, we do not expect a single soft-phonon mode but rather modifications of many phonons, resulting from the unstable size of the Sm ion.

Since $Sm_{0.75}Y_{0.25}S$ is an alloy, there will also be effects on the phonons from the mass disorder of the system. By comparison with other alloy systems,[21] these alloy effects are small compared to the large effects observed in this system. Specifically, single-site mass-defect coherent-potential-approximation (CPA) calculations[21] would predict identical phonon widths for the LA and TA modes of the same energy, whereas we find the LA up to four times broader than the TA. There is a flat dispersionless mode at about 5 THz. Mass-defect calculations show that this is about the expected position for the yttrium local mode. In systems with a discrete localized mode, the band modes are only slightly affected by the mass disorder. Other than the appearance of the localized mode, we do not expect the lattice dynamics to be altered significantly except for a possible contribution to the phonon widths due to local inhomogenieties.

The full phonon-dispersion curves are necessary for a microscopic understanding of the lattice dynamics. We have made least-squares fits to the data using a screened rigid-ion model.[22] This model will, in fact, fit a LA [111] mode that is below the TA [111] and then place the LO modes below the TO. However, the unusual dispersion of the LA [111] mode can not be well fit and therefore more elaborate models are needed to describe the data. Bilz has pointed out that the breathing-shell model[23] should be directly applicable to the intermediate-valence system and he and his associates are in the process of applying this model to our data. The charge-fluctuation model of Wakabayashi[24] should also be appropriate for the intermediate-valence problem. This model correctly predicts that the TA modes should be much narrower than the LA and that the phonon widths should be a maximum in the region of greatest phonon softening. The virtue of the breathing-shell and charge-fluctuation models is that they go beyond the adjustment of force constants and allow the Sm-ion size to change.

Temperature-dependent phonon measurements have been made for some of the acoustical modes.

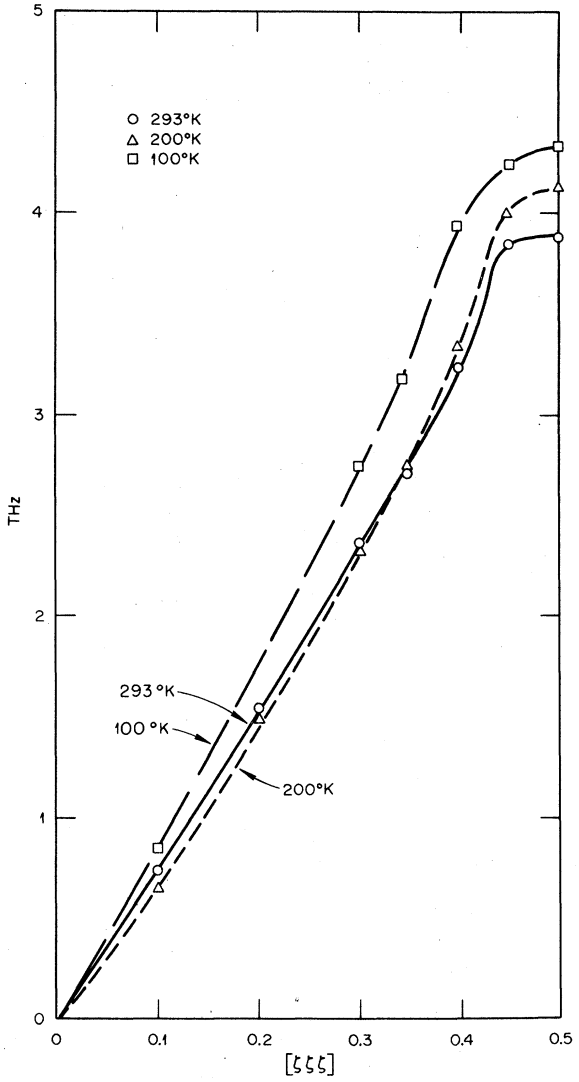

FIG. 2. Temperature dependence of the [111] longitudinal acoustical-phonon branch. The errors in frequency are not bigger than the data points at 0.1 of the zone boundary but become as large as 0.1 THz at 0.4 of the zone boundary as is shown in Fig. 1.

Particular attention has been centered on the modes in the [111] direction. It is found that the TA branch remains essentially unchanged (±0.02 THz) in its position as a function of temperature but that the LA branch is quite temperature dependent. Figure 2 shows the LA [111] mode at three temperatures. This branch has the weakest slope and the largest curvature at 200 K, which is the center of the smooth transition in lattice constant and valence. The phonon linewidths are also largest at 200 K. For example, at $q = 0.3$ of the [111] zone boundary, the widths are 0.90

THz at 100 K, 1.25 THz at 200 K, and 0.86 THz at 293 K. The LA modes in the other directions are also temperature dependent but less so than the LA [111].

The bulk modulus at room temperature, obtained from ultrasonic measurements[12,13] on a different sample of $Sm_{0.75}Y_{0.25}S$, is 0.71×10^{11} dyn/cm^2. Our phonon data at low q yield a bulk modulus of $(0.79 \pm 0.1) \times 10^{11}$ dyn/cm^2 in excellent agreement with the ultrasonic measurements. We find the bulk modulus is softest at the 200-K transition temperature, with a value of $(0.53 \pm 0.1) \times 10^{11}$ dyn/cm^2 and stiffens considerably at 100 K where it is $(1.6 \pm 0.1) \times 10^{11}$ dyn/cm^2. The bulk modulus of the alloy is considerably smaller than that for either SmS (4.8×10^{11} dyn/cm^2) or YS (10.0×10^{11} dyn/cm^2) which shows the intermediate-valence character of $Sm_{0.75}Y_{0.25}S$ at all temperatures. Changing the temperature provides a way of confirming that the anomalous phonon properties are related to the intermediate valence, since we know that the lattice constant, and hence the valence, changes with temperature.

The acoustical modes[15] of divalent semiconducting SmS appear quite normal for a material with the rocksalt structure. YS is a metal which becomes superconducting below about 2.8 K.[25] The [111] LA phonons[16] lie well above the TA phonons except near the zone boundary where there is a dip in the LA phonon branch similar to that seen in other superconductors. It is obvious from Fig. 1 that the phonon dispersion we observe in $Sm_{0.75}Y_{0.25}S$ is not a combination of the properties of its integral valence constituents, SmS and YS. We conclude that the anomalous phonon properties we observe are associated with the intermediate-valence state.

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