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Phonon anomalies at the valence transition of SmS: An inelastic x-ray-scattering study under pressure

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The phonon dispersion curve of SmS under pressure was studied by inelastic x-ray scattering around the pressure-induced valence transition. Between 0 and 0.9 GPa, a significant softening of the longitudinal acoustic modes propagating along the [111] direction was observed spanning a wide q region from $(2\pi/3a, 2\pi/3a, 2\pi/3a)$ up to the zone boundary. The largest softening occurs at the zone boundary. At higher pressures up to 7.6 GPa, these phonon modes become much less pressure sensitive, whereas the low q modes display a significant hardening. This phonon spectrum indicates favorable conditions for the emergence of pressure-induced superconductivity in SmS.

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In the past decades, a rich variety of condensed-matter phenomena (high-temperature superconductivity, giant magnetoresistance, heavy fermion ground state) has been attributed to the interplay between charge, lattice, and magnetic degrees of freedom. Pressure is a unique tool to tune the different couplings between these parameters. One spectacular achievement of the past years is the pressure-induced nonconventional superconductivity observed at the quantum critical point of several heavy fermion systems.[1,2] While spin fluctuations are generally believed to be responsible for the Cooper pairing in these compounds, superconductivity is enhanced near the charge instability of some of them.[3] This motivated us to reinvestigate intermediate valence compounds where the charge fluctuations are at their strongest, and in particular the case of SmS.[4] At ambient pressure, SmS is a semiconductor which crystallizes in the NaCl structure (black phase) with a divalent Sm^{2+} ionic configuration $(4f^6)$. At 0.65 GPa (at room temperature), it undergoes a first-order isostructural phase transition[5] to a metallic state (gold phase). In this phase, the Sm ion has an intermediate valence achieved by promoting a $4f$ electron into the conduction band: $Sm^{2+} \leftrightarrow Sm^{3+} + 5d$. In contrast to the room-temperature behavior, the semiconducting state persists at $T=0$ up to $P_\Delta = 2$ GPa, where the sample ultimately becomes metallic.[6] It is expected that, near P_Δ or at still higher pressure, a magnetic quantum critical point will be reached when the Sm ion approaches its trivalent state. The search for the related magnetic order and possible superconductivity in good samples is certainly an experimental challenge. In this paper, we focus on the lattice dynamics of SmS under pressure using inelastic x-ray scattering (IXS). IXS presents several advantages here over inelastic neutron scattering (INS), since it can be carried out on micron-sized samples contained in a diamond anvil cell (DAC), and does not require isotopic substitution for Sm. This permitted us to extend previous INS data obtained on the same system at the border of the technique[7] to much higher pressure (7.6 GPa in the present case, while the INS experiments was limited to 0.7 GPa), while keeping a good crystal quality in the whole pressure range. The present study focuses on the longitudinal acoustic (LA) phonon dispersion curve along the [111] direction. For the first time, a significant softening of the LA[111] mode is observed at the zone boundary (ZB) at the valence transition. At higher pressures, a hardening of the low and intermediate q modes occurs while the mode frequencies in the ZB vicinity do not evolve further. This provides indications of favorable conditions for the emergence of superconductivity in SmS at high pressure.

A $150\times100\times40$-μm^3 platelet of SmS, oriented with its surface normal parallel to the $[1\bar{1}0]$ direction, was cut in the extensively studied batch[6] grown two decades ago by Holtzberg using the Czochralskyi method. The sample was loaded in a rhenium gasket placed in a DAC, using methanol-ethanol 1:4 as pressure transmitting medium. The DAC was then oriented such that the [111] direction was lying in the horizontal scattering plane. The pressure was measured on-line by the conventional ruby fluorescence technique. The IXS measurements were carried out on the undulator beamline ID28 at the European Synchrotron Radiation Facility, Grenoble. The incident beam is monochromatized by a perfect plane Si-crystal working in extreme backscattering geometry at the (9,9,9) reflection (17.794 keV). The monochromatic beam is then focused onto the sample position by a toroidal mirror in a 250×80-μm^2 spot. The scattered photons are analyzed by a bank of five spherically bent high-resolution Si analyzers placed on a 7-m-long horizontal arm. The analyzers are held one next to the other with a constant angular offset and operate in backscattering geometry at the same reflection order. The energy (ω) scans are performed by varying the monochromator temperature while keeping the analyzer crystals at fixed temperature. The instrumental energy resolution achieved in this configuration is 3 meV. The cell was mounted in a vacuum chamber positioned on the sample stage in order to reduce the scattering by air. Measurements were carried out at room temperature in transmission geometry near the $\tau=(2,2,2)$ and $\tau=(3,3,3)$ Bragg reflections. This choice is a compromise between the benefit gained by working at the highest momen-

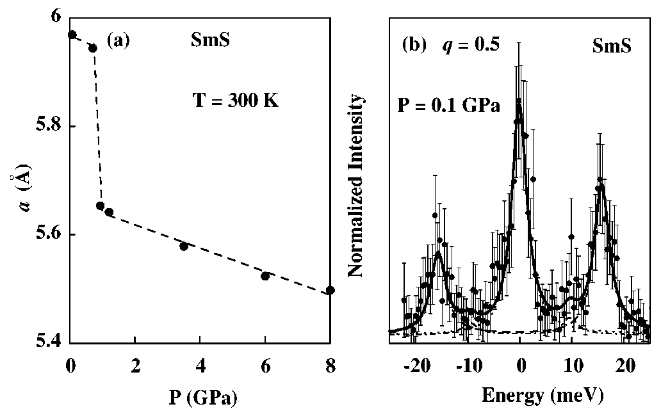

FIG. 1. (a) Pressure variation of the lattice parameter a of SmS at $T=300$ K. (b) IXS spectrum measured at $\mathbf{q}=(0.5,0.5,0.5)$ for $P=0.1$ GPa at $T=300$ K. The lines are fit to the data including a central peak, a TA mode, and a LA mode, as explained in the text.

tum transfer ($\mathbf{Q}$) possible because of the essentially Q^2 dependence of the IXS cross section and the limited angular opening of the pressure cell. Furthermore, these ($\mathbf{Q},\omega$) regions were free from contamination by the diamond phonon branches. The measurement of the LA [111] modes was achieved by having $\mathbf{q}$ // $\mathbf{Q}$ // [111] where $\mathbf{q}$ is the reduced wave vector $\mathbf{q}=\mathbf{Q}-\tau$, which will be expressed in the following as $\mathbf{q}=(q,q,q)$ with q in reciprocal lattice units (r.l.u.). In fact, the longitudinal condition was only fulfilled by one of the five analyzers, while the four others point to slightly different directions in q space leading to a nonnegligible transverse component. Transverse components were also observed in the pure longitudinal configuration due to the finite q resolution and the crystal mosaicity.

The valence transition of SmS was monitored by the pressure-dependence of the lattice parameter measured on the (2,2,2) Bragg reflection as shown in Fig. 1(a). A drastic reduction of about 5% occurs at the valence transition. The overall behavior is consistent with previously reported measurements using x-ray diffraction in the same pressure range.[9] The sample mosaicity estimated by the full width at half maximum of the (2,2,2) Bragg reflection rocking curve increases from 0.12° at 0.1 GPa to 0.33° at 7.6 GPa. This demonstrates that the crystal quality is still good even at high pressure, the volume collapse at the transition being often destructive for SmS samples. The phonon spectra were measured for each pressure point at two or three different crystal orientations corresponding to ten or 15 q values for the complete set of analyzers. A typical energy scan (± 25 meV) took about 5 h. The data were normalized to the monitor intensity. The high-pressure spectra were further normalized to the intensity of the elastic peak (diffuse scattering centered at $\omega=0$) at low pressure. Both the Stokes and anti-Stokes parts of the spectra were fitted with Lorenztian weighted by the Bose thermal population factor, after deconvolution by the resolution function. The central contribution was also fitted by a Lorenztian. This is illustrated in Fig. 1(b) at $\mathbf{q}=(0.5,0.5,0.5)$ for $P=0.1$ GPa at $T=300$ K. Within the accuracy of our measurement, all the phonon peaks were found to be resolution limited.

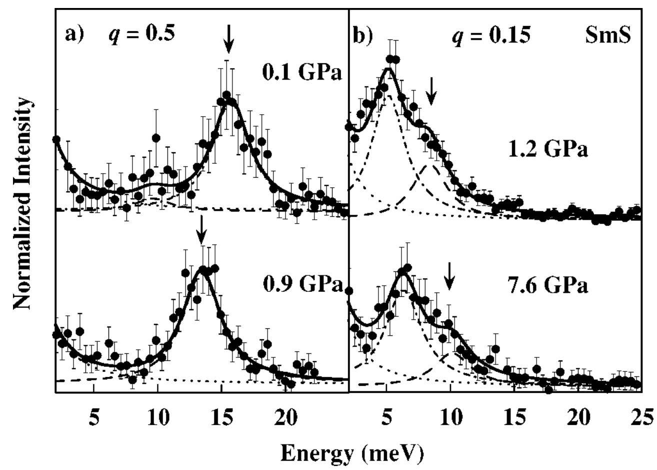

FIG. 2. IXS phonon spectra of SmS measured (a) at $\mathbf{q}=(0.5,0.5,0.5)$ before ($P=0.1$ GPa) and after ($P=0.9$ GPa) the valence transition at $T=300$ K. (b) At $\mathbf{q}=(0.15,0.15,0.15)$ for $P=1.2$ and 7.6 GPa at $T=300$ K. The lines are fit to the data as explained in the text. The dotted line corresponds to the central peak, the dot-dashed line to the TA modes and the dashed one to the LA modes. The arrows indicate the position of the LA[111] modes.

The spectra measured on both sides of the valence transition at $P=0.1$ and 0.9 GPa at the [111] zone boundary are shown in Fig. 2(a). A clear softening from 15.7 to 13.4 meV can be observed. In contrast, a subsequent hardening occurs in the low and intermediate q regions when pressure is further increased. This effect is illustrated in Fig. 2(b) at $q=0.15$ r.l.u. for $P=1.2$ and 7.6 GPa. At this low q value, the transverse component (dot-dashed line) is strongly enhanced essentially because of the mosaicity increase after the valence transition. The overall dispersion curves of the LA [111] modes as a function of pressure obtained after fitting are summarized in Fig. 3. The IXS data at $P=0$ are in com-

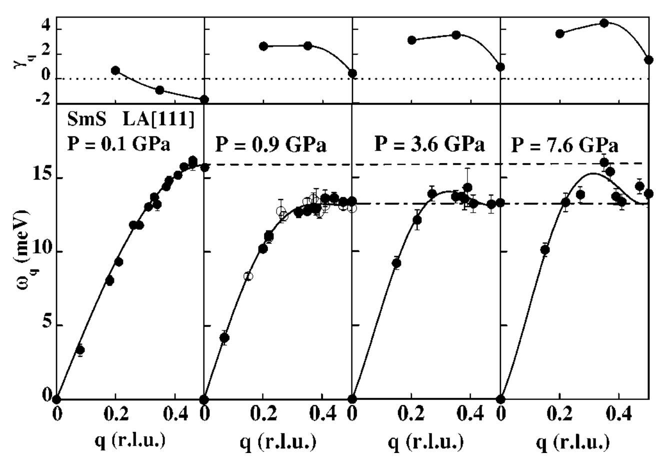

FIG. 3. Dispersion relation ω_q obtained for the LA [111] branch of SmS at $T=300$ K for several pressures. Lines through the points are guides for the eyes. The open circles in the second panel correspond to data obtained at 1.2 GPa. The dashed line and the dot-dashed line shows the ZB value at ambient and high pressures, respectively. The upper part shows the variation with q of the mode Grüneisen parameter γ_q. The dotted line indicates $\gamma_q=0$.

TABLE I. Sound velocities in the black (or semiconducting) and gold (or metallic) phases and shifts in the phonon frequency in the [111] direction for $Sm_{0.75}Y_{0.25}S$, SmS and YS compounds. The upper and lower parts of the table, respectively, are related to the low- and high-pressure phases of SmS, respectively. The range of the physical parameters where the shift is observed is given in parentheses. For YS, the shift between the ionic model (I.M.) and the experimental results (expt.) is considered.

	v_{black} (ms^{-1})	v_{gold} (ms^{-1})	$\Delta\omega$ $q=0.35$ r.l.u. (%)	$\Delta\omega$ at $q=0.5$ r.l.u. (%)
SmS (INS) (Ref. 7)	4300		−40 (0–0.7 GPa)	+17 (0–0.7 GPa)
SmS (INS) (Ref. 8)	4000			
SmS (IXS, low P)	3700		−11 (0–0.9 GPa)	−17 (0–0.9 GPa)
$Sm_{0.75}Y_{0.25}S$ (INS) (Ref. 10)	2900 (100 K)	2600 (300 K)	−19 (100–300 K)	−11 (100–300 K)
SmS (IXS, high P)		5100	+14 (0–7.6 GPa)	−17 (0–7.6 GPa)
YS (INS) (Ref. 18)		5500	−25 (I.M.-expt.)	−88 (I.M.-expt.)

plete agreement with the previous measurements made in the black phase,[7,8] and there is in particular a good reproducibility of the sound velocities. The sound velocity deduced from the initial slope of the dispersion changes from 3700 ms^{-1} at $P=0.1$ GPa to 5100 ms^{-1} at $P=7.6$ GPa. The softening of the phonon frequencies in the upper q-region occurs at the valence transition from $q\approx 1/3$ r.l.u. up to the ZB. Above 0.9 GPa, the mode frequencies in the ZB vicinity no longer change with pressure. The overall behavior of the LA[111] modes is summarized in the pressure variation of the mode Grüneisen parameter γ_q defined as $\gamma_q=-\partial \ln \omega_q/\partial \ln V$ (V being the unit cell volume). Given the strong volume change at the transition, γ_q was estimated for each q value by fitting $ln \omega_q$ to a polynomial as a function of $\ln V$. The result is shown in the upper part of Fig. 3. At low pressure, γ_q changes sign halfway to the ZB. It becomes zero at the ZB after the valence transition occurs. Finally it increases for each q value at higher pressure.

The softening of the LA [111] mode observed at 0.9 GPa is found to extend over a large q range up to the ZB. In contrast, the ZB value was not found to soften in the INS study limited to 0.7 GPa. In order to understand this point, it is useful to describe the data obtained on a related system, $Sm_{1-x}Y_xS$, where a similar valence transition occurs through Y doping at about $x=x_c=0.15$. Among this series of compounds, $Sm_{0.75}Y_{0.25}S$ in particular was extensively studied by INS,[10,11] transport and thermodynamic measurements.[4] At room temperature this compound is equivalent to SmS at $P\approx 1$ GPa with an intermediate valence state with 30 at. % of Sm^{2+}. On cooling, it undergoes a valence transition at 200 K back into a state similar to the one of SmS at $P=0$.[12] The INS studies performed on this compound show anomalously soft LA[111] modes at 300 K which lie below the TA[111] modes except at the ZB. Between the (nearly) integer valence state (100 K) and the valence transition (200 K), the highest softening is obtained at $q\approx 1/3$ r.l.u. similarly to the INS measurements in SmS between 0 and 0.7 GPa. But on heating further up to 300 K, while this mode frequency does not further evolve, the ZB mode continues to soften leading to a situation similar to SmS at 0.9 GPa, as shown by our IXS data. When put altogether, the temperature dependence of the phonon spectrum in $Sm_{0.75}Y_{0.25}S$ and the pressure dependence in SmS indicates that features characteristic of the mixed valence state, the nearly integer valence state and the transition region can be clearly identified in the phonon dispersion curve. This is the case in $Sm_{0.75}Y_{0.25}S$, where the three different regimes were studied at 100, 200 and 300 K. On the other hand, the INS study of SmS under pressure was limited to the transition region ($P=0.7$ GPa) while the present IXS work is mostly devoted to the metallic phase up to high pressure ($P=7.6$ GPa). The respective sound velocities and phonon frequency shifts measured in the [111] direction by INS on the $Sm_{1-x}Y_xS$ system along with the IXS results on SmS are reported in Table I, emphasizing the most important result of our study, namely that the softening, observed between 0 and 0.9 GPa at the [111] ZB, is of the same order as that observed in $Sm_{0.75}Y_{0.25}S$ between 100 and 300 K.

At high pressures, our data exhibit an important hardening at low q as expected for a normal metal. Unfortunately no ultrasonic measurements are available in SmS under high pressure due to the formation of microcracks in the samples which prevent the measurement. Detailed ultrasonic measurements are limited to the black phase,[13] and show a general softening linked to the approach of the phase transition. Nevertheless, the large increase under pressure of the bulk modulus B measured by x-ray diffraction up to 7 GPa is a good indication that phonon stiffening is expected.[9] For a cubic system, the bulk modulus is expressed as $B=(c_{11}+2c_{12})/3$ and the sound velocity in the [111] direction is $v=\sqrt{(c_{11}+2c_{12}+4c_{44})/3\rho}$ where c_{ij} are the elastic constants and ρ is the material density. Since c_{44} is determined by the TA[100] modes which are not believed to be strongly pressure dependent,[7,13] the bulk modulus and the [111] sound velocity should exhibit similar pressure dependence.

On the theoretical side, several works aimed at calculating the phonon spectrum after the INS measurements performed on $Sm_{0.75}Y_{0.25}S$ either by using microscopic models or more phenomenological methods.[14–17] General arguments predict the location of the phonon anomaly:[15] The valence transition induces a change of volume of the Sm ion that will at first affect the motion of the surrounding next-nearest-neighbor S atoms. Volume fluctuations occur in the longitudinal channel and in the [111] direction corresponding to the highest packing. Most of the models reproduce a softening halfway to the ZB since the zone boundary corresponds to Sm only motion.

They are clearly not sufficient to explain our new results which show that also the ZB LA[111] mode is soft at the valence transition. It is useful to note that the shape of the LA[111] phonon we measured at 7.6 GPa is qualitatively similar to the one of the superconducting compound YS (Ref. 18) (see Table I). The softening at $q=0.5$ r.l.u. in this compound is thought to be related to a high density of states of *d* electrons at the Fermi level.[16] Soft phonon modes and a high density of states at the Fermi level favorize superconductivity as calculated in the strong coupling theory.[19] Such a scenario was already invoked for the other isostructural binary alloy NbC.[20,21] In Table I, the phonon frequency shift for YS is given relative to a theoretical calculation without electron-phonon coupling. One can formulate the hypothesis that pressure induces, in parallel to (or in cooperation with) the change of valence of SmS, an increased density of states at the Fermi level which produces the anomaly at $q=0.5$ r.l.u.

Our IXS data obtained under pressure in SmS exhibit a softening of the LA[111] mode from halfway and up to the ZB when entering the metallic phase. This softening effect is maximum at the [111] ZB. The ZB LA[111] phonon energy does not evolve further up to 7.6 GPa, while a gradual hardening of the low and intermediate *q* modes occurs in parallel. This latter effect is to be linked to the unusual strong pressure dependence of the bulk modulus of SmS in the metallic phase. The former softening effects are attributed to the electron-phonon interaction occurring at the valence transition of SmS and probably to an increasing density of states at the Fermi level at high pressure. Future studies aimed at finding pressure-induced superconductivity in SmS are encouraged by the large phonon anomalies which persist up to high pressure where the Sm valence has certainly reached an integer value, and by the probable appearance of a magnetic phase opening also the possibility of spin fluctuation mediated pairing.

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[12] This temperature induced valence transition is not completely equivalent to the case of SmS under pressure since the ground state of $Sm_{0.75}Y_{0.25}S$ at $T=0$ is still mixed valent (with 80 at. % of Sm^{2+}).

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