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. 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 as SmS becomes metallic. The largest softening occurs at the zone boundary and stays stable up to the highest measured pressure of 80 kbar while a gradual hardening of the low q modes simultaneously appears. 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 non-conventional 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 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 Sm2+ ionic configuration (4f0). At 6.5 kbar (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: Sm2+↔Sm3+ + 5d. The semiconducting state persists at T=0 up to PΔ=20 kbar where the sample ultimately becomes metallic [6]. It is expected that, near PΔ 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. This permitted us to extend previous INS data obtained on the same system [7] at the border of the technique to much higher pressure (80 kbar in the present case, while the INS experiments was limited to 7 kbar), 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. The IXS measurements show a strong hardening of the LA modes close to the zone center with increasing pressure while for the first time, significant softening is observed at the zone boundary and persists far above the valence transition. This provides indications of favorable conditions for the emergence of superconductivity in SmS at high pressure.

A 150×100×40 μm3 platelet of SmS was cut in the extensively studied batch [7] grown two decades ago by F. Holtzberg using the Czochralsky method. The direction [110] was normal to the surface so to have the three principal axis in the surface plane. The sample was then loaded in a rhenum gasket placed in a DAC, using methanol-ethanol 1:4 as pressure transmitting medium. The pressure was measured on-line by 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 μm2 spot. The scattered photons are analyzed by a bench 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 momentum transfer ($Q$) possible because of the essentially $Q^2$ dependence of the IXS cross section and the limited angular opening of the pressure cell. Furthermore, these $(Q,\omega)$ regions were free from contamination by the diamond phonon branches. The measurement of the LA [111] modes was achieved by having $q=Q-\tau$, which will be expressed in the following as $q=(q,q,q)$ with $q$ in reciprocal lattice unit (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 non-negligible 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 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 0.12º at 0.7 kbar to 0.33º at 80 kbar. 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 2 or 3 different crystal orientations corresponding to 10 or 15 $q$-values for the complete set of analyzers. Typical energy scan ($\pm 25$ meV) took about 5 hours. 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 Lorentzian weighted by the Bose thermal population factor, after deconvolution by the resolution function. The central contribution was also fitted by a Lorentzian. This is illustrated in Fig. 2b at $q=(0.5,0.5,0.5)$ for $P=0.7$ kbar at $T=300$ K. Within the accuracy of our measurement, all the phonon peaks were found to be resolution limited.

The spectra measured on both sides of the valence transition at $P=0.7$ and 9.3 kbar at the [111] zone boundary (ZB) are shown in Fig. 2b. A clear softening from 15.7 to 13.4 meV can be observed. When pressure increases, a subsequent hardening occurs in the low and intermediate $q$ regions. This effect is illustrated in Fig. 2b at $q=0.15$ r.l.u. for $P=12$ and 80 kbar. 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 complete agreement with the previous measurements made in the black phase [8] and there is in particular good reproducibility of the sound velocities. The sound velocity deduced from the initial slope of the dispersion changes from 3700 ms$^{-1}$ at $P=0.7$ kbar to 5100 ms$^{-1}$ at $P=80$ kbar. The softening of the phonons frequencies in the upper $q$-region occurs from $q \approx 1/3$ r.l.u. up to the ZB. At the ZB, the softening starts at 9 kbar and does not further evolve, once the valence transition has occurred. The overall behavior of the LA[111] modes is summarized in the pressure vari-

![FIG. 1: (a) Pressure variation of the lattice parameter $a$ of SmS at $T=300$ K. (b) IXS spectrum measured at $q=(0.5,0.5,0.5)$ for $P=0.7$ kbar at $T=300$ K. The lines are fit to the data including a central peak, a TA and a LA mode as explained in the text.](image1)

![FIG. 2: IXS phonon spectra of SmS measured (a) at $P=0.7$ kbar and (b) at $P=9.3$ kbar 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.](image2)
ation of the mode Grüneisen parameter $\gamma_q$ defined as
$\gamma_q = -\partial \ln \omega_q / \partial \ln V$ ($V$ being the unit cell volume) and
shown in the upper part of Fig. 3. At low pressure, $\gamma_q$
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 at $P > 9$ kbar 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 7 kbar. In order to understand this
apparent discrepancy between the INS and IXS data, it is
useful to describe the data obtained on a related system,
$\text{Sm}_{1-x}\text{Y}_x\text{S}$, where a similar valence transition oc-
curs through Y doping at about $x = x_c = 0.15$. Among
this series of compounds, $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ in particular was
tensively studied by INS [10, 11], transport and ther-

modynamic measurements [12] since it allows one to study the
intermediate valence state by chemical pressure. At
room temperature this compound is equivalent to $\text{SmS}$
at ambient and high pressure respectively. The upper part
shows the variation with $q$ of the mode Grüneisen parameter
$\gamma_q$. The dotted line indicates $\gamma_q = 0$.

On the theoretical side, several works aimed at calculat-
ing the phonon spectrum after the INS measurements
performed on $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ either by using microscopic
models or more phenomenological methods [14, 15, 16, 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. Vol-
ume 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 mo-
tion. They are clearly not sufficient to explain our new
results which show that also the ZB LA[111] mode is soft
at high pressure. It is useful to note that the shape of the
LA[111] phonon we measured at 80 kbar is qualitatively
similar to the one of the superconducting compound YS
[18] (see Table I). The softening at $q = 0.5$ r.l.u. in this

dependence of the phonon spectrum in $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ and
the pressure dependence in $\text{SmS}$ show distinct features
for the mixed valence state, the nearly integer valence
state and the transition regions. In order to sort out the
different observed effects, we report in Table I the
sound velocities and the phonon frequency shifts mea-
sured in the [111] direction by INS on the $\text{Sm}_{1-x}\text{Y}_x\text{S}$
system along with the IXS results on $\text{SmS}$.

At high pressures, our data exhibit an important hard-
ening at low $q$ as expected for a normal metal. Unfortu-
nately no ultrasonic measurements are available in $\text{SmS}$
der high pressure due to the formation of microcracks in
the samples which prevent the measurement. Detailed
ultrasonic measurements are limited to the black phase
[18] 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 70 kbar is a good indication that phonon
stiffening is expected [19]. For a cubic system, the bulk
modulus expresses as $B = (c_{11} + c_{12})/3$ and the sound ve-

locity in the [111] direction is $v = \sqrt{(c_{11} + c_{12} + 2c_{44})/3\rho}$
where $c_{ij}$ are the elastic constants and $\rho$ is the material
density. Since $c_{44}$ is determined by the TA[100] modes
which are not believed to be strongly pressure dependent
[18], the bulk modulus and the [111] sound velocity
should exhibit similar pressure dependence. As seen in
Table I $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ is much more compressive and not a
good starting point for a discussion of the sound veloc-
ities in $\text{SmS}$ under pressure.

The most important result of our study is the soften-
ing at the [111] ZB which is of the same order as the
one observed in $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ at $q = 0.5$ r.l.u. between 100
and 300 K. One possible interpretation of the discrep-
ancy between the INS and IXS data obtained in $\text{SmS}$
derunder pressure is that the INS results were limited to the
transition or near-transition region ($P = 7$ kbar) while the
present IXS data were extended well within the metallic
phase.

On the theoretical side, several works aimed at calculat-
ing the phonon spectrum after the INS measurements
performed on $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ either by using microscopic
models or more phenomenological methods [14, 15, 16, 17].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{dispersion.png}
\caption{Dispersion relation $\omega_q$ obtained for the LA [111]
branch of $\text{SmS}$ 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 12 kbar.
The dashed line and the dot-dashed line shows the ZB value
at ambient and high pressure respectively. The upper part
shows the variation with $q$ of the mode Grüneisen parameter
$\gamma_q$. The dotted line indicates $\gamma_q = 0$.}
\end{figure}
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 respectively lower part of the table is related to the low and respectively high pressure phases of SmS. The range of the physical parameters where the shift is observed is given in parenthesis. For YS, the shift between the ionic model (I.M.) and the experimental results (exp.) is considered.

| Compound          | $v_{\text{black}}$ (ms$^{-1}$) | $v_{\text{gold}}$ (ms$^{-1}$) | $\Delta \omega$ | $q=0.35$ r.l.u. | $\Delta \omega$ at $q=0.5$ r.l.u. |
|-------------------|---------------------------------|--------------------------------|------------------|------------------|----------------------------------|
| SmS (INS)         | 4300                            |                                | -40 (0-7 kbar)   | +17 (0-7 kbar)   |
| SmS (INS)         | 4000                            |                                | -11 (0-9 kbar)   | -17 (0-9 kbar)   |
| SmS (IXS, low P)  | 3700                            |                                | -19 (100-300K)   | -11 (100-300K)   |
| Sm$_{0.75}$Y$_{0.25}$S (INS) | 2900 (100 K) | 2600 (300 K) | +14 (0-80 kbar) | -17 (0-80 kbar)  |
| SmS (IXS, high P) | 5100                            |                                | -25 (I.M.-exp.)  | -88 (I.M.-exp.)  |
| YS (INS)          | 5500                            |                                |                  |                  |

compound is to be related to a high density of states of $d$ electrons at the Fermi level [14]. Soft phonon modes and high density of states at the Fermi level favorize superconductivity as calculated in the strong coupling theory [14]. Such scenario was already invoked for the other isostructural binary alloy NbC [20, 21]. In Table I, the phonon frequency shift for YS is given relatively to a isostructural binary alloy NbC. In Table I, the phonon frequency shift for YS is given relatively to a isostructural binary alloy NbC. Such scenario was already invoked for the other isostructural binary alloy NbC. In Table I, the phonon frequency shift for YS is given relatively to a isostructural binary alloy NbC.

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. This scenario reinforces the idea that the INS data obtained on SmS under pressure represents phenomena around the transition while the present IXS data characterizes the metallic phase up to high pressure and thus exhibits new anomalies in the phonon spectrum.

Our IXS data obtained under pressure in SmS exhibit a softening of the LA [111] mode from halfway and up to the ZB as soon as the metallic phase is reached. This softening, maximum at the [111] ZB is unchanged up to 80 kbar while 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 also 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 the possibility of spin fluctuation mediated pairing.

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