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X-RAY ABSORPTION STUDY OF THE PRESSURE-INDUCED VALENCE TRANSITION OF SmS

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L_{III}-absorption spectra were measured for SmS under truly hydrostatic pressure up to 7.50 kbar at room temperature. Values for the mean valence were derived from the double-peaked L_{III}-edge, and nn Sm-S and Sm-Sm distances were obtained from an analysis of the EXAFS structure, both as a function of pressure. The latter scale well with lattice constants from previous high-pressure X-ray diffraction work. A slight pressure-induced change of the mean valence was already observed in the black semiconducting phase, and the semiconductor-metal transition - which is not completed for the studied sample at 7.50 kbar - was found to be smeared over a pressure range of ≈2 kbar. The analysis of the EXAFS spectra supports one threshold energy and one nn Sm-S distance even in the mixed-valent regime. A critical damping of the EXAFS amplitude was observed in the region of the phase transition.

1. INTRODUCTION

SmS has long been considered a prototype of rare-earth systems with an unstable valence, since the Sm-valence can easily be changed both by external pressure and by chemical substitution /1/. When exposed to a pressure of about 7 kbar black semiconducting SmS (NaCl structure) undergoes a supposedly first-order electronic transition to an isostructural golden mixed-valent phase accompanied by a volume collapse of ≈14%. Information on the mean Sm valence in the collapsed phase had previously been obtained from lattice constant measurements /1,2/ and Sm-149 Mössbauer isomer shift studies with relatively low resolution /3/. Recently, a further second-order phase transition to a metallic regime was postulated from a study of electric transport properties /4,5/.

A detailed study of the mean Sm valence as a function of pressure is highly desirable in order to clarify the high-pressure phase diagram of SmS. We have therefore studied L_{III}-absorption spectra of SmS as a function of hydrostatic pressure up to 7.50 kbar. The mean valence was obtained from the structure of the double-peaked L_{III}-edge, and the distances from the central atom to the nn-S and nn-Sm atoms were derived from an analysis of the EXAFS oscillations. Thus both mean valence and lattice parameter can be simultaneously measured for a given sample, allowing a unique check on the validity of Vegard's law, which has been used extensively in deriving mean valences from lattice constant data /6/.

Mixed-valent systems are known to possess strong phonon anomalies due to the large difference in ionic radii associated with the two valence states as well as due to comparable magnitudes of the valence-fluctuation and phonon frequencies /7,8/. X-ray absorption experiments - due to their short characteristic measuring time of the order of 10^{-16} sec - reflect the instantaneous situation concerning valence as well as distances from the absorbing atom to the neighbouring shells. Strong effects of the mentioned phonon anomalies in mixed-valent materials are therefore expected in the EXAFS spectra, which, however, have not been observed in recent experiments on TmSe /9/ and $Sm_{0.75}Y_{0.25}S$ /10/. It may be expected that a study of SmS in the black semiconducting and the high-pressure golden mixed-valent phase at the *same temperature* provides a much clearer check on this question.

2. EXPERIMENTAL DETAILS

The X-ray absorption experiments were performed in transmission geometry at the spectrometer ROEMO at HASYLAB (DESY Hamburg) using a Si(111) double-crystal monochromator optimized for small harmonic content /11/, which provided a tunable X-ray beam with a total width of ∿1.6 eV at 6.7 keV. During the experiments the electron-storage ring DORIS was operated at 2.2 GeV and about 40 mA electron current. The incident photon flux was recorded with a He-filled ionization chamber, while the transmitted X-ray inten-

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sity was determined by single-photon counting using an argon-filled proportional counter for minimizing contributions from higher harmonics. The studied absorber was prepered from a single crystal of SmS, which was finely powdered under argon atmosphere and subsequently pressed into paraffin for better homogeneity. The high-pressure experiments were performed at room temperature under hydrostatic conditions employing an oil-pressure cell equipped with two Be-windows. Ambient-pressure data were also taken with the absorber cooled to liquid-nitrogen temperature.

3. RESULTS AND DATA ANALYSIS

Figure 1 shows some typical L_{III}-edge absorption spectra of SmS at room temperature and various hydrostatic pressures. The 1.11-kbar spectrum as well as the ambient-pressure spectrum (not shown here) exhibit prominent peaks at the L_{III}-threshold ("white line"), which arise from transitions from atomic $2p_{3/2}$ core levels into empty 5d states with a high density of states at the Fermi level /12,13/. The energetic position of the prominent peak in the 1.11-kbar spectrum (and also in the ambient-pressure spectrum), is characteristic for divalent samarium /14,15/. In addition, a weak peak shifted by 7.2±0.02 eV to higher binding energy is already observed in the ambient-pressure and the 1.11-kbar spectrum, which arises from trivalent Sm in the sample. This 7-eV shift of the peaked L-edge is due to an increase of the $2p_{3/2}$-core electron binding energy when the $Sm^{2+}-4f^6$ configuration changes to $Sm^{3+}-4f^5$ /16/. It cannot be clarified presently whether the weak Sm^{3+} contribution, which has been observed in all SmS samples studied so far by L-egde spectroscopy /15,10/ is due to bulk Sm^{3+} impurities in the sample, or to the grinding procedure, or to an intrinsic mixed-valent behaviour of SmS.

The dramatic effects of hydrostatic pressure on the electronic properties of SmS in the region of the semiconductor-metal transition are clearly visible in the spectra of Fig. 1. Starting at a pressure slightly above 6 kbar, the Sm^{3+}/Sm^{2+} intensity ratio increases with pressure, which means that an increasing proportion of Sm atoms is found in the $Sm^{3+}-4f^5$ configuration during the 10^{-16} sec exposure time of the L_{III}-edge measurement. On the other hand, no changes in the positions of the Sm^{2+} and Sm^{3+} white lines are observed as a function of pressure within the present accuracy.

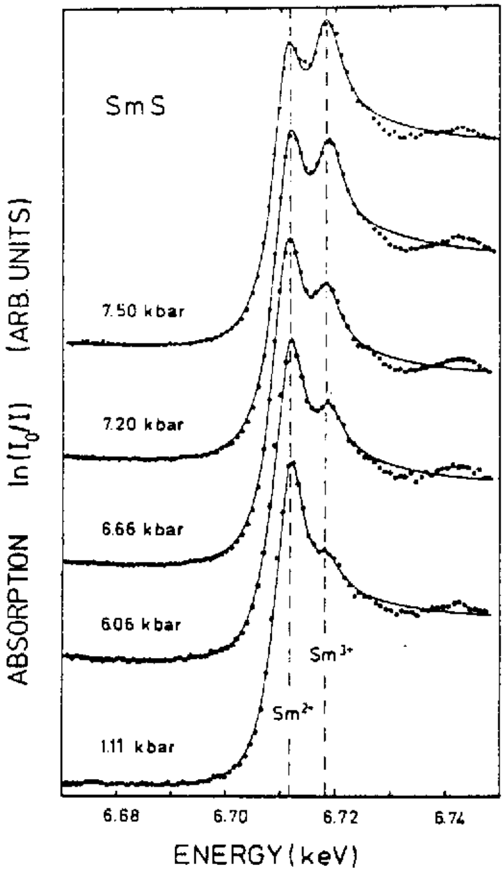

Figure 1: Sm L_{III}-edge absorption as a function of photon energy for SmS at various hydrostatic pressures. The solid lines represent the results of least-squares fit analyses as described in the text.

In order to derive values for the mean valence $\bar{v}$ a superposition of two identical L_{III}-edge profiles, set equal to the sum of a Breit-Wigner-Fano function plus an arctan function, was least-squares fitted to the experimental data points /17/. The line-shape parameters were determined from the 1.11-kbar spectrum and kept constant in the fits of the other spectra. Almost identical values for the intensities of the Sm^{2+} and Sm^{3+} subspectra resulted from least-squares fits with Lorentzian profiles for the white lines. The solid lines in Fig. 1 represent the results of the Breit-Wigner-Fano profile analyses, and the obtained values for the mean valence $\bar{v}$ are plotted in Fig. 3a as a function of pressure. We observe that the mean valence of the studied SmS sample increases from 2.12±0.05 at ambient pressure to a value of 2.42±0.05 at the highest reached pressure of 7.50 kbar. Previous studies of lattice constants /2/ and Mössbauer isomer shifts of SmS /3/ under pressure indicated values for v around 2.7 at pressures slightly above the semiconductor metal transition. This suggests that the transition is not completed in the studied SmS sample at the highest pressure applied in the present work.

We have also investigated the EXAFS structure of the X-ray absorption coefficient above the Sm-L_{III} edge for SmS as a function of pressure. Representative room temperature results are displayed in Fig. 2 for two pressures, namely

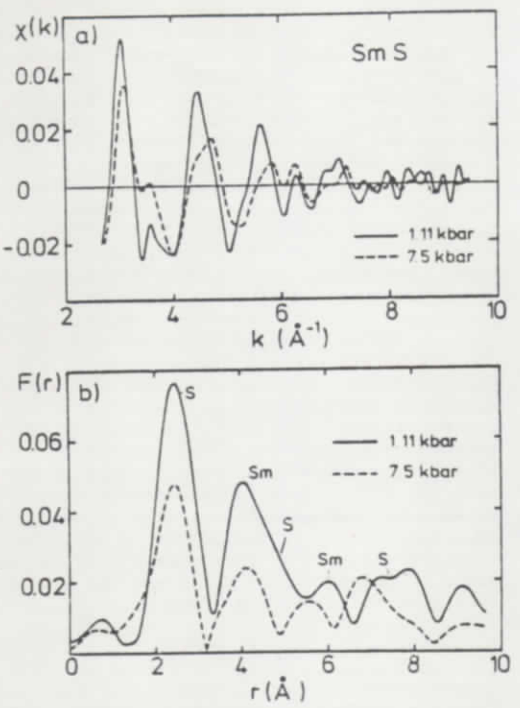

Figure 2: (a) EXAFS-spectra $\chi(k)$ of SmS after background removal at pressures of 1.11 kbar (solid curve) and 7.50 kbar (dashed curve), respectively. (b) Fourier transforms $F(r)$ in distance space of $k^3\chi(k)$ for the two cases.

1.11 kbar (solid lines) and 7.50 kbar (dashed lines). The observed EXAFS spectra $\chi(k)$ clearly show an increase in the lengths of the periods in k-space corresponding to a reduction of the interatomic distances. The magnitude $F(r)$ of the Fourier transform of $k^3\chi(k)$ is shown for the two pressures in Fig. 2b. As indicated in the figure, the nearest five neighbouring sulfur and samarium shells, known from the rocksalt structure of SmS, can be clearly assigned to the observed peaks in $F(r)$. With increasing pressure the peaks in $F(r)$ shift to lower distances. We also observe a quite drastic decrease of the magnitude of $F(r)$ with pressure (to be discussed later).

The EXAFS spectra were analyzed in the usual way by Fourier filtering techniques as described e.g. in Ref. /18/. Because of the relatively low statistical accuracy of the high-pressure EXAFS data, the small Debye-Waller factors at room temperature, and a possible influence of multiscattering processes, only the nn and nnn shells were analyzed. The k-dependent Sm-S scattering phases were obtained from an analysis of the 77-K EXAFS spectrum of SmS at ambient pressure and the known nearest neighbour Sm-S distance under these conditions /1/. From the argument of chemical transferability these scattering phases are expected to be independent of pressure and valence. They were therefore used to derive the pressure dependence of the nn Sm-S distance shown in Fig. 3b. The agreement with the results of the previous X-ray diffraction measurements of Keller et al. /2/ is very good (within ±0.02 Å). This comparison again shows that the semiconductor-metal transition is not fully completed in our SmS sample at 7.50 kbar.

The EXAFS spectra could be evaluated best with a single zero of kinetic energy for the photoelectrons, even though the observed L-edge structures suggest 7-eV differences for photoelectrons originating from Sm^{2+} and Sm^{3+}. This finding is in agreement with the results of other EXAFS studies of mixed-valent compounds /9,10/. We also could not detect two different nn Sm-S distances in the observed EXAFS spectra, which would lead to a beating of the Fourier-filtered nn-shell EXAFS oscillations /19/. This again is in accord with the previous EXAFS studies of mixed-valent systems /9,10/. The statistics of the present high-pressure data is not good enough to decide on this question also for the nn Sm shell.

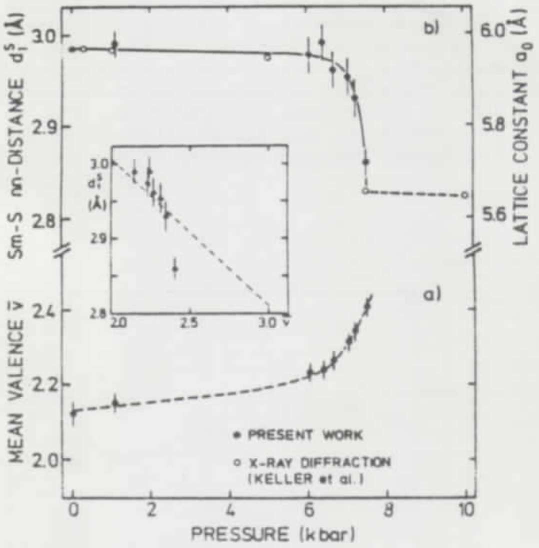

Figure 3: Pressure dependence of (a) the mean valence $\bar{v}$ of SmS derived from an analysis of the L_{III}-edge spectra and (b) of the Sm-S nn-distance d_1^S obtained from the EXAFS spectra. Also shown in (b) are values derived from the X-ray diffraction work of Ref. /2/. In the insert d_1^S is plotted as a function of the mean valence $\bar{v}$. The dashed line represents Vegard's law.

A clear damping of the magnitude of the Fourier transform F(R) is observed at 7.50 kbar as compared to 1.11 kbar (see Fig. 2b). This may be described by an attenuation factor, which is usually accounted for by a Debye-Waller-type term $\exp(-2\sigma_j^2k^2)$ in the EXAFS expression for $\chi(k)$ /18/. The mean-square average of the difference of displacements σ_j^2 between the atoms in the j-th coordination shell and the central atom may have contributions from thermal vibrations and static disorder. We have analyzed the attenuation factor for the nn-S shell as a function of pressure by comparison with the 77-K ambient-pressure EXAFS spectrum using the procedure of Ref. /20/. This leads to the difference $\Delta\sigma^2=\sigma_{300}^2(P)-\sigma_{77}^2(0)$ of the mean-square displacements of the nn-S distances between the room temperature high-pressure and the 77-K ambient-pressure data. The results of this analysis are presented in Fig. 4. In the semiconducting phase the disorder clearly gets smaller up to a pressure of $\approx$6 kbar, which may be expected from a stiffening of the lattice. At the phase transition a pronounced increase of $\Delta\sigma^2$ is observed, with a peak at $\approx$7.20 kbar. At the highest pressure studied (7.50 kbar) $\Delta\sigma^2$ has again decreased. It cannot be decided from the present data whether this increase in $\Delta\sigma^2$ at the phase transition is due to the known phonon anomalies in mixed-valent systems or simply due to some static disorder. The observed decrease of $\Delta\sigma^2$ at the highest pressure point indicates a dominant contribution from static disorder at the phase transition. Such an effect has to be expected if the sample undergoes a first-order phase transition smeared out by inhomogeneity effects in the sample. A clarification of this question has to wait for an extension of the hydrostatic pressure range to higher pressures.

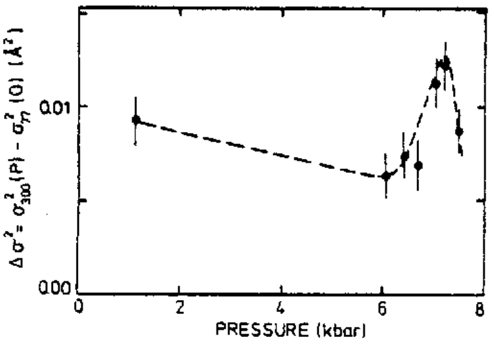

Figure 4: Difference $\Delta\sigma^2$ of nn Sm-S mean-square displacements between the 300-K high-pressure and 77-K ambient pressure data.

4. DISCUSSION

The L_{III}-edge spectra reveal a small Sm^{3+}-derived structure even at ambient conditions as can be seen e.g. in the 1.11-kbar spectrum presented in Fig. 1. The intensity of this trivalent peak was found to vary only slightly for the different samples studied. The lowest Sm^{3+} content was found to be $\approx$12% corresponding to a mean valence of $\bar{v}\approx2.11$ at ambient conditions. Presently it cannot be decided whether this is due to Sm^{3+} impurities in SmS (either intrinsic or created by grinding) or if it reflects a mixed-valent behaviour of SmS already at ambient conditions. The impurity hypothesis is supported by the fact that sample-dependent Sm^{3+}-impurity phases have been identified in various SmS crystals by other methods /21/. On the other hand, recent high-resolution VUV-photoemission experiments on SmS(100) surfaces failed in detecting any Sm^{3+}features in the observed valence bands /22/. In these latter measurements, however, a bulk mixed-valent state of Sm close to divalency would hardly be seen due to the high surface sensitivity and an expected surface-valence transition /22,23/. In order to clarify the addressed question, L-edge measurements on thin single-crystalline discs of SmS should be performed and are in fact planned in the near future.

The results for $\bar{v}$ displayed in Fig. 3a also show that a small change of the 4f occupation number occurs already in the black phase before the semiconductor-metal transition takes place. This is in agreement with a recent theoretical description of the semiconductor-metal transition of SmS in terms of f-d hybridization in the semiconducting phase /24/. A slight increase of the mean Sm valence with pressure in the black phase had previously also been suggested on the basis of the results of high-pressure Mössbauer experiments /3/.

The semiconductor-metal transition of the studied SmS sample seems to be smeared over a pressure range of more than 2 kbar (see Fig. 3). This may be due to an inhomogeneous distribution of transition pressures for the first-order phase transition in our powdered sample. Such an interpretation is supported by the fact that a variation of the transition pressure had already previously been found in X-ray diffraction studies of several SmS samples under hydrostatic pressure /2/. It should be possible to clarify the true nature of the transition by an extension of the present pressure range keeping the truly hydrostatic conditions.

The present X-ray absorption experiments allow a simultaneous determination of the mean valence (from the L-edge structure) and the nn Sm-S distance d_1^S (from EXAFS) as a function of pressure. Since we have found $a_0=2d_1^S$ to hold for all pressure values (see Fig. 3b), a plot of d_1^S versus $\bar{v}$ allows a unique check on the validity of Vegard's law. The data plotted in the insert of Fig. 3 despite the limited accuracy exhibit a considerable deviation from a linear relationship and show that a linear interpolation of a measured lattice constant would lead to a too large value for $\bar{v}$. The dashed line in the insert of Fig. 3 represents Vegard's law assuming d_1^S=2.81 Å for a fictitious $Sm^{3+}S$ and $\bar{v}$=2.11 for SmS under ambient conditions (d_1^S=2.98 Å). The above statement would also hold if the deviation of $\bar{v}$ from 2.0 for SmS under ambient conditions is due to Sm^{3+} impurities. Then the dashed line has to end at d_1^S= =3.01 Å for $\bar{v}$=2.0, and all experimental $\bar{v}$ values would have to be shifted by 0.11. The observed deviation from Vegard's law is in qualitative agreement with other findings and has recently been interpreted on the basis of the bulk modulus in the intermediate-valent regime /6/.

Finally, a few words should be made about the reliability and accuracy of the $\bar{v}$ values derived from L-edge spectra of mixed-valent systems. The central question is to what extent the observed double-edge structure of the L-edge represents the initial-state valence mixture. There is strong support from a variety of experimental data that in heavy rare-earth systems, where the 4f-states are well localized, a possible influence of final-state screening effects is negligible. This is qualitatively understandable, since in an L_{III}-edge absorption process the electron is excited into a rather localized 5d-state so that the positive core-hole is well screened with respect to the more itinerant valence and conduction electrons, thus making a major redistribution of these electrons unprobable. The situation is quite different in deep core-hole XPS measurements, where the initially unscreened positive core-hole has been found to cause both shake-up and shake-down processes, which may completely masque the initial-state valence /25,26/. It should be noted that such final-state effects have also not been identified up to now in valence-band photoemission spectra of heavy rare-earth systems /27/. We would like to emphasize that these arguments may not apply to the case of Ce systems /28/.

It is therefore reasonable to assume that the observed double structure of the L_{III}-edge reflects the initial-state valence. The *absolute accuracy* of the derived mean valence, however is subject to some uncertainty, since it depends to some extent on the line-shape analysis, particularly due to the broad features of the L-edge white lines (caused mainly by lifetime effects). We have employed the same lineshape parameters for the Sm^{2+}- and the Sm^{3+}-derived edge structures even though a lower intensity of the white line may be expected for the Sm^{3+} ion due to a locally partly-filled d state. If this should be the case the values for $\bar{v}$ have to be considered as lower limits.

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