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HIGH PRESSURE STUDIES OF SmSe AT 77 K

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Résumé

Nous avons mesuré des spectres EXAFS de SmSe à haute pression (jusqu'à 57 kbar) et à basse température (77 K) avec une résolution spatiale élevée. Les spectres au seuil K de Se montrent que les fluctuations dans la distance Sm-Se s'accroissent environ 0.05 Å lorsque le composé passe à travers sa phase de valence intermédiaire. La transition de valence, qui est isostructurale et continue, commence à 25 kbar. Pour réaliser ces mesures nous avons construit un dispositif pour usage à haute pression et basse température. La cellule de haute pression est montée dans l'orientation axiale.

Abstract

EXAFS studies with high spatial resolution have been performed at the Se K-edge edge of SmSe at 77 K and up to 57 kbar. An increase in the fluctuation of the Sm-Se bond length of ~0.05 Å is observed upon going through the isostructural mixed valent transition which is continuous and begins at 25 kbar. For these measurements a pressure cell was constructed for use at low temperature. It is used in the axial geometry.

Introduction

In this paper high pressure x-ray absorption spectroscopic studies are extended to low temperatures. This permits the study of effects that do not occur at room temperature and, through the reduction of thermal motion has the advantage of providing improved resolution of physical phenomena studied at higher temperature. Firstly, we describe the high pressure cell designed for low temperature. Secondly, we present results on the pressure-induced mixed valence transition in SmSe.

At room temperature SmSe undergoes a continuous valence transition with pressure, showing a large decrease in volume while retaining the same NaCl structure [1,2]. This has been studied at room temperature with x-ray absorption spectroscopy [3]. The L3-edge of Sm involves dipole-coupled transitions from initial 2p states to final d-symmetry. In SmSe the high density of empty d-states near the Fermi energy results in strong white lines for the Sm2+ and Sm3+ states. The white line of Sm3+, which corresponds to a higher binding energy, is chemically shifted relative to Sm2+ by ~7 eV. By fitting each peak to a Lorentzian convolved with a Gaussian, the effective valence shown in Fig. 1 is obtained as a function of pressure. This study revealed two features. The collapse in volume occurs at a lower pressure than the valence change. Both the Sm L3- and Se K-edge EXAFS show that the Debye-Waller factor $\alpha_1^2$ for the nearest neighbour shell appears to increase and then decrease on going through the transition, despite the large decrease in n.n. distance $R_1$. 

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The studies of SmSe were extended to low temperature to examine further these features. The Se K-edge is of particular interest because of the enhanced spatial resolution possible. At 77 K the Se EXAFS is still observed at $k = 24 \text{ Å}^{-1}$ whereas the maximum value at the Sm L$_3$-edge is restricted to 12.5 Å$^{-1}$ due to the onset of the L$_2$ absorption edge. The Se K-edge also enables one to answer the question whether or not its Debye-Waller factor contains an additional component reflecting changes in Sm backscattering amplitudes due to the different electronic configurations of the Sm$^{2+}$ and Sm$^{3+}$ states.

**Experimental**

Our high pressure cell uses the axial geometry in which the x-ray beam passes through the anvils (Fig. 2). This has the advantage that the sample cross-sectional area is unaffected by pressure and its thickness changes in a controlled way, but precludes the use of diamond anvils since their Bragg diffraction may contaminate the EXAFS spectra. Boron carbide (B$_4$C) anvil inserts are used. Due to their lower hardness, as compared to diamond, the anvil tips have a diameter of 2 to 3 mm, and thus require large forces for compression. At room temperature we have used B$_4$C anvils to generate pressures up to 150 kbar.

The pressure cell is intended for use at liquid helium temperatures. Therefore the pistons are driven purely mechanically rather than hydraulically as in earlier work at ambient temperature [4]. The pressure cell resembles the diamond anvil cell by Syassen and Holzapfel [5], except that due to the larger anvil tip area it has to generate much larger forces (up to 130 kN). The cell is constructed from a maraging steel (VascoMax T-250) which is easily machined in the soft condition and can be hardened by simple heat treatment without distortion.
The compression of the inconel gasket (G) and the sample is effected by the turning of two gear-set threaded spindles (T) which through a bracket (B) and strut (S) mechanism move the anvils (A) towards each other. The turning is accomplished by a retractable ratchet which is connected through the cryostat wall to the spur gear (SG). This design gives a large force multiplication so that the torque required for turning the spindles is relatively small.

In order to determine the pressure, a material of known equation of state is included in the gasket with the sample and its EXAFS is measured. In the present work, the pressure calibrant was RbCl. Due to uncertainty in the P-V relation at 77 K, the pressure could be determined to only ±3 kbar.

X-ray absorption measurements were made on the Se K-edge of SmSe on beamline IV-1 at the Stanford Synchrotron Radiation Laboratory. At low temperatures and high pressures there is a significant increase in the amplitude of the EXAFS interference function and its Fourier transform due to the reduction in the Debye-Waller interference factor (Fig.3).

Discussion

We find that the distribution of n.n. Sm and second n.n. Se about Se are each described adequately at all pressures at 77 K by a single Gaussian distribution function. Also $R_2 = \sqrt{2} R_1$ as expected for the NaCl crystal structure. This is in agreement with other EXAFS results [6,7,8] which have shown for homogeneous mixed valent materials that all the atoms take a single-average position rather than dynamically distorted distributions with two different stable positions corresponding to the two valence states of the Rare Earth ion. This is attributed to a large electronic hybridization energy which reduces the dependence of the anion on the valency of the Sm ions [9].

As shown in Fig. 4 there is an increase in the SmSe Debye-Waller factor $\sigma_1^2$ in the pressure range 25 to 50 kbar at 77 K. It has been suggested that a similar increase in $\sigma_1^2$ observed at the pressure-induced mixed valent transition in SmS may contain a dominant contribution from static disorder wherein the first-order phase transition is smeared out by inhomogeneity effects in the sample [8]. This is not significant in the case of the broader continuous transition in SmSe. The maximum increase in $\sigma_1^2$ which occurs at the middle of the mixed valent transition implies a difference between the nearest neighbour distances Sm$^{2+}$-Se and Sm$^{2+}$-Se of 0.045 Å, close to the value estimated by Kohn et al [9].

Finally the large k-space range of the Se K-edge EXAFS has permitted a quantitative measurement of the Sm backscattering amplitude f(k). We find that f(k) for Sm$^{2+}$ obtained from pressures below the mixed valent transition differs in the range 6 to 9 Å$^{-1}$ from that for Sm$^{3+}$ obtained at higher pressures. There is also a related change in the Se-Sm phase shift $\delta(k)$ in the same range.
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