

Rigid covalent bond of α -sulfur investigated via temperature-dependent EXAFS

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1 Introduction

Sulfur (S) is a member of the chalcogen group in the periodic table that exhibits a hierarchical structure where primary and secondary structures coexist. α -Sulfur (α -S) is the stable phase of S at room temperature where atoms form crown-shaped eight-membered rings through covalent bonds (primary structure), the rings stack via weak interactions (secondary structure). In Selenium, the covalent bonds become shorter upon melting contrary to other materials which is caused by the absence of inter-chain interactions. By investigating the covalent bonding within α -S we can gain valuable insights into the strength and nature of the covalent bonding, how it is affected by the inter-ring interactions, and the structure-property relationship in chalcogen group of elements.

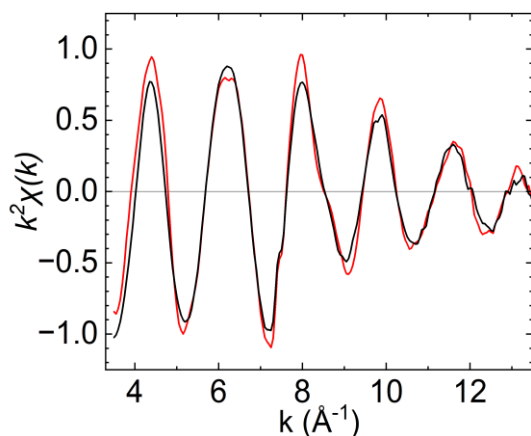


Fig. 1: $k^2\chi(k)$ of α -S at 10 K (red) and 300 K (black).

Achieving this goal requires a high-precision experimental technique capable of providing detailed structural information. X-ray absorption fine structure (XAFS) spectroscopy emerges as a promising method, offering element-specific and high-precision information that can elucidate the covalent bond length (r_{CB}), coordination numbers (N), and mean-square relative displacement (MSRD) in α -S. Moreover, extended XAFS (EXAFS) gives us information about the strength of atomic correlations, making it particularly effective in studying chalcogen elements where strong primary and weak secondary structures coexist. XAFS studies on S often rely on conversion electron yield (CEY) and fluorescence methods. However, the CEY measurements cannot be performed at low temperatures as it requires gas to flow around the sample and the fluorescence method is hindered

by self-absorption. In addition, the energy of the S-K edge is quite low at 2.472 keV. At this energy, there is significant absorption of X-rays by everything in the path, including air. To our knowledge, there have been no report of low-temperature EXAFS measurements of S. We overcame these challenges by performing measurements in vacuum in transmission mode using a photodiode (PD). In this report, we present the first results for the low-temperature EXAFS of α -sulfur.

2 Experiment

The sample for the XAFS measurements was a thin S film. S of 99.999% purity obtained from NewMet was deposited on a sheet of multi-walled carbon nanotubes (MWCNTs) in vacuum conditions (pressure of 3.0×10^{-6} Torr). Raman spectroscopy was used to confirm the crystal form of the sample by comparing the obtained spectrum with reference standards.

XAFS measurements for S-K edge (2.472 keV) were performed with a soft x-ray mode at the BL-9A beamline in the Photon Factory of High Energy Accelerator Research Organization (KEK-PF), Tsukuba, Japan. An ionization chamber was used to detect the incident X-rays and a Si p-intrinsic-n photodiode (HAMAMATSU S14605) detector was used for detecting the transmitted X-rays. The sample was attached to a cryostat holder in a vacuum chamber equipped with a 7.5 μm Kapton window which enabled measurements at temperatures as low as 10 K. The samples were measured across temperatures ranging from 10 to 300 K, where the temperature of the sample was monitored by a T-type thermocouple. The X-rays passed through the Kapton window and the sample before finally reaching the PD detector. This configuration achieved an overall transmittance exceeding 25% across the entire measurement energy range, enabling XAFS measurement of the S-K edge in transmission mode.

The EXAFS data were analyzed using the miXAFS program [1]. The $\chi(k)$ functions were extracted from the raw data using the AUTOBK method [2] with the R_{bkg} parameter set to 1 \AA . The $\chi(k)$ were then Fourier transformed ($|\text{FT}(r)|$) using a Hamming window in the range of 4.0–13.5 \AA^{-1} . Two prominent peaks were observed in the $|\text{FT}(r)|$ at 2.05 and 3.35 \AA , which were attributed to the first nearest neighbor (1NN) and second nearest neighbor (2NN) correlations within the chain, respectively. The second peak was significantly attenuated with an increase in temperature, whereas the first peak remained nearly unchanged. This suggests that the covalent bonding

is strong but the bond angle is flexible. To extract $\chi(k)$ for the 1NN atomic correlations, the first peaks in the Fourier transform (r-space) in the range of 1.35 Å–2.70 Å were inverse Fourier transformed. Finally, the Fourier filtered $k^2\chi(k)$ data were fitted in k-space with the conventional theoretical EXAFS equation using the non-linear least squares method to obtain structural parameters.

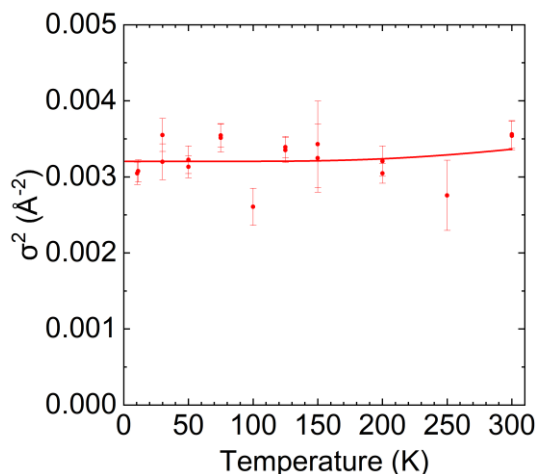


Fig. 2: The temperature variation of the MSRD for the covalent bond of α -S K edge (red). The solid lines show the Einstein model fitting.

3 Results and Discussion

The $\chi(k)$ functions for α -S are presented in Fig. 1. A surprising feature is that there is no significant attenuation at high temperatures, even in the high- k region, which has not been observed in conventional materials. Additionally, r_{CB} was almost constant at 2.054 ± 0.007 Å across the measured temperature range of 10–300 K, contrary to expectations for conventional materials. These findings suggest an exceptionally strong covalent bond in α -S.

To quantify this further, the temperature variation in the MSRD was examined, which reflects the extent of thermal vibration between atoms and is indicative of the strength of atomic interactions. Fig. 2 shows the temperature variations in MSRD for the covalent bond of α -S. The temperature variation is extremely small compared to those for other materials, suggesting that the covalent bond of α -S is quite strong. Einstein model fitting for the temperature variation in the MSRD provided the Einstein temperature of 942 K, which corresponds to a force constant of 405 Nm^{-1} . The value of the force constant is about three and five times larger than those of t-Te and t-Se, respectively. This further shows the strong nature of the α -S covalent bond. Moreover, the average value of the asymmetric parameter (C_3) of EXAFS was $-1.4 \pm 2.5 \times 10^{-5} \text{ Å}^{-3}$. This is practically zero, implying that the potential of the covalent bond is also highly symmetric.

Although these results may seem unusual compared to typical materials, they can be understood by considering the specific characteristics of chalcogen elements and the unique structure of α -S. In general, chalcogen elements have covalent bonds that are stronger than the inter-ring/chain interactions. In α -S, the covalent bond strength

is further amplified by the absence of overlap between lone pair and antibonding (σ^*) orbitals on adjacent rings, unlike what is seen in t-Se and t-Te.

References

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