

A natural abundance ^{77}Se solid-state NMR study of inorganic compounds

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ABSTRACT

Various inorganic selenium-based compounds were analysed by ^{77}Se solid-state NMR, and a distinct difference in chemical shift ranges for compounds where selenium is present as selenide (Se^{2-}) ionically and covalently bonded systems was observed. The selenides exhibit a shift range of approximately -700 to -100 ppm, as opposed to 700 to 1600 ppm for the compounds where there tends to be more direct covalent bonding to the selenium. The anisotropic hyperfine shift observed in NbSe_2 is shown to be axially symmetric, where the H_{11} component is found to be normal to the Se_3 -trigonal plane.

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1. Introduction

Selenium (Se) belongs to the chalcogens and is known for being a toxic element because of its ability to replace sulphur in proteins [1,2]. In materials science, Se plays a vital role in photosensitive semiconductors [3], and is also used as an additive for colouring glasses [3]. Despite the diverse applications of Se, direct characterisation of Se is often difficult because of the non-crystalline nature of many solid materials. In such materials it can be difficult to gain definitive, unambiguous information about the local structure of selenium via X-ray diffraction (XRD) and electron microscopy (SEM and TEM). Nuclear magnetic resonance (NMR) spectroscopy is one of the principal techniques used to characterise physical, chemical and structural information around a target nucleus. For selenium, ^{77}Se (nuclear spin-1/2 and 7.58% natural abundance) is the only NMR-active isotope. Due to the large chemical shift range (~ 3000 ppm) found for ^{77}Se , the application of solution-state ^{77}Se NMR to organoselenium materials is well documented [3]. Unfortunately many materials cannot be readily studied by ^{77}Se solution NMR because of their solid nature. For this reason, solid-state ^{77}Se NMR is a potentially very important method for the characterisation of selenium sites directly. Despite the technique's potential it has still been relatively little used because of the difficulty in acquiring ^{77}Se NMR signals from solid samples.

Even with an intermediate Larmor frequency 19.1 MHz (corresponding to 100 MHz for ^1H), ^{77}Se is still a relatively little studied

nucleus in solid-state NMR spectroscopy because of other unfavourable nuclear properties. Although not suffering from quadrupole broadening effects [4], it can exhibit very long spin-lattice (T_1) relaxation times of up to hundreds of seconds. Moreover, the modest natural abundance of ^{77}Se also creates a signal-to-noise (S/N) challenge to probe the selenium sites. To overcome the aforementioned challenges, cross-polarisation (CP) experiments have been used with materials containing ^1H and ^{31}P [5]. The spin magnetisation transfer during the CP period can enhance the ^{77}Se signal by up to a factor of $\sim \gamma(i)/\gamma(^{77}\text{Se})$, and can also shorten the relaxation period required in the experiment [6]. Solid-state ^{77}Se NMR has also successfully been used on materials containing paramagnetic species (NbSe_2 and TiSe_2) [7,8], where the ^{77}Se spin-lattice relaxation becomes much more efficient (less than 0.1 s).

In the current study, a limited series of simple inorganic selenium-containing compounds, that were being used to demonstrate the practicality of solid-state ^{77}Se NMR spectroscopy for a broader range of more complex selenium containing materials, are characterised by ^{77}Se NMR. The new data collected here makes a significant addition to the ^{77}Se solid-state NMR data reported in the literature and a comparison is made to other literature data.

2. Experimental procedure

Selenium-containing samples were purchased from Alpha Aesar (NbSe_2 (99.8%), CdSe (99.995%), K_2SeO_4 (99.5%), Na_2SeO_4 (99.9%) and SeO_2 (99.4%)) and from Ventron (ZnSe (99.999%)). The samples were used without purification. All ^{77}Se magic-angle spinning (MAS) NMR spectra, except for NbSe_2 , were recorded on

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a Chemagnetics Infinity spectrometer operating at a frequency of 68.88 MHz, equipped with a 8.45 T Oxford Spectrospin magnet. A Doty 4 mm HX probe was used with sample spinning at 12 kHz. A single pulse excitation (30°) experiment was carried out with a pulse delay of up to 600 s, depending on the sample. In the case of NbSe₂, the spectra were acquired at ambient temperature on a Chemagnetics Lite spectrometer operating at a frequency of 39.04 MHz, equipped with a Magnex 4.79 T magnet. The MAS NMR spectrum was acquired with sample spinning at 14.1 kHz. Both MAS and static NMR spectra were recorded with a 30° – 60° spin-echo experiment with a pulse delay of 0.1 s. The total acquisition times for all ⁷⁷Se NMR spectra range from 2 to 24 h. ⁷⁷Se NMR spectra were referenced to (CH₃)₂Se by setting the sharp MAS signal of solid ZnSe to -362 ppm. The ⁷⁷Se spectral simulation for NbSe₂ was done with QuadFit [9] and Simpson [10].

3. Results and discussion

The selenium compounds of interest were classified into three different groups: (1) compounds with stronger covalent bonds to selenium which includes selenates and hydrogen selenites, (2) those with ionic selenide (Se²⁻) species and (3) with paramagnetic species. The ⁷⁷Se NMR spectra are shown in Figs. 1 (groups 1 and 2) and 2 (group 3), and the NMR results are summarised in Table 1, together with literature data from similar compounds. For both groups 1 and 2, the ⁷⁷Se MAS NMR spectra exhibit similar sharp featureless signals with line widths ranging from 40 to 450 Hz; however, the isotropic chemical shift ranges (δ_{iso}) are clearly different. ⁷⁷Se δ_{iso} for the selenides are generally found to appear at lower field compared to those for the more covalently bonded compounds. The difference in ⁷⁷Se can be attributed to the fact that the selenium sites consist of different bonding characteristics with the neighbouring atoms. The compounds with Se–O bonding consist of stronger covalent bonds (with typical bond lengths of ~ 1.6 Å) where the Se bonding electrons are more readily delocalised through covalent bonds, and result in higher δ_{iso} . In the case of the ionic selenides, the main contribution to the ionic bond (where typical bond lengths are ~ 2.5 Å) is the ionic interaction between the Se anion and the local cation. The more negative δ_{iso} may be attributed to the presence of d-shell electrons from the cation.

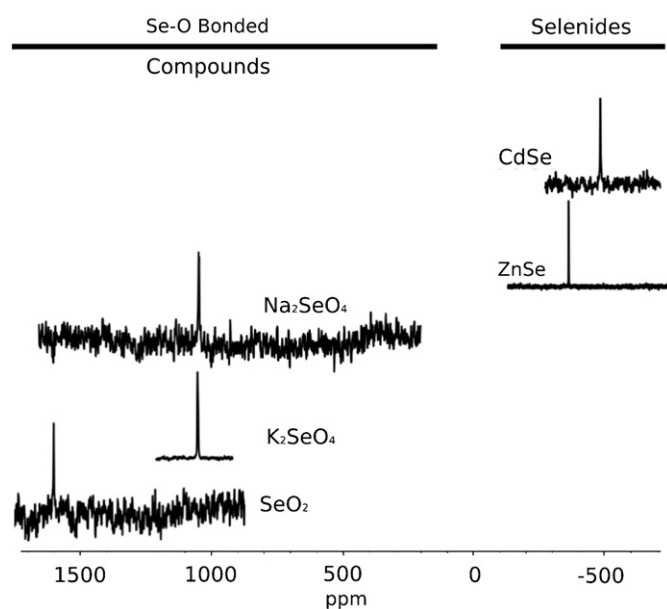


Fig. 1. ⁷⁷Se solid-state MAS NMR spectra taken at 8.45 T.

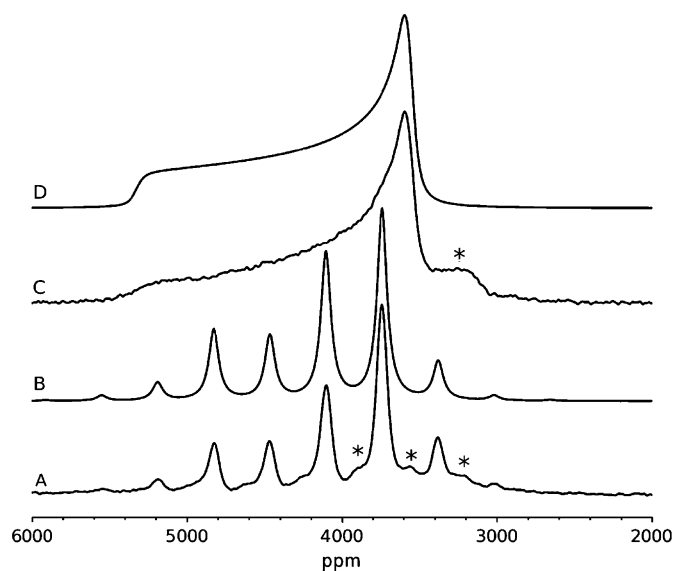


Fig. 2. Experimental (A,C) and simulated (B,D) ⁷⁷Se MAS (A,B) and static (C,D) NMR spectra for NbSe₂ at 4.79 T. The asterisks indicate an impurity.

Much work was published during the 1970s on NbSe₂ using ⁹³Nb [31] and ⁷⁷Se [7] NMR as NbSe₂ displays charge density waves (CDWs) below 35 K [32] and is a superconductor below the critical temperature of 7.1 K [33]. Although ⁷⁷Se NMR has been reported on NbSe₂, the recent advances of NMR spectroscopy has meant that the newly acquired spectra are of much higher quality and thus more accurate NMR information can be obtained. The neighbouring Nb(IV) is a paramagnetic ion due to an unpaired 4d electron, which can induce a paramagnetic shift in the ⁷⁷Se signal. Furthermore, NbSe₂ is also a conductor [34], the conduction electrons can give rise to a Knight shift. The paramagnetic Nb(IV) and its conduction electrons interact with the ⁷⁷Se nucleus via the hyperfine interaction [35]. The Knight and paramagnetic shifts are both hyperfine interactions and as such are difficult to distinguish. Therefore, it is possible that the previously published figures [36] for Knight shift could be affected by a paramagnetic shift and it is safer to assume that these figures are actually hyperfine shifts. Borsa et al. [7] have reported the two extremes of the powder pattern at $0.226 \pm 0.003\%$ and $0.395 \pm 0.01\%$. The spectrum obtained here (Fig. 2) shows that the interaction is axially symmetric. The information from Borsa et al. and the knowledge that the interaction is axially symmetric gives an isotropic hyperfine shift of $H_{\text{iso}} = 0.338\%$ and a span of the anisotropic hyperfine shift of $H_{\text{W}} = H_{11} - H_{33} = 0.169\%$. The value of H_{W} is very similar to that measured here, 0.171%; however, the value of H_{iso} is significantly different to the value measured here of 0.412%. The difference in the two values of H_{iso} is likely to be due to the difficulties in referencing in the original work. Dupree et al. [8] reported an ⁷⁷Se isotropic Knight shift (K_{iso}) for an isostructural compound, TiSe₂ and found it to be 0.111%. The fact that H_{iso} for NbSe₂ is significantly larger than K_{iso} for TiSe₂ is because of the paramagnetic effect from Nb(IV) and of the different electronic susceptibility in NbSe₂. Despite the large overall linewidth (~ 2000 ppm) observed in both MAS and static NMR spectra (Fig. 2), the spectra show excellent S/N ratio compared to those for the non-paramagnetic compounds, and this enabled low levels ($< 5\%$) of an Se-impurity to be revealed, as shown by intensity at ~ 3200 ppm in the static spectrum. The improved S/N is attributed to the presence of paramagnetic Nb(IV) and conduction electrons, which result in efficient relaxation of ⁷⁷Se allowing for fast signal averaging and hence more averages are possible in a fixed time.

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