Determination of the chemical shift tensor of ^{77}Se in a selenious-acid crystal

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By cross-polarization of ^{77}Se nuclei with protons we obtained high-resolution NMR spectra of ^{77}Se in a selenious-acid crystal. The principal components and the direction cosines of the chemical-screening tensor of the ^{77}Se nuclei were determined.

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Nuclear magnetic resonance (NMR) of rare nuclei in solids are being successfully investigated by the double pulse resonance method proposed by Pines *et al.*[1] By now, the magnetic screening of the nuclei ^{13}C, ^{29}Si, and ^{15}N, which have a small natural abundance, has been studied in a large number of compounds,[2] in many of which the chemical-shift (CS) tensors were determined. The screening of the ^{77}Se nuclei (natural abundance 7.5%) was investigated, apart from in liquids, only in single-crystal metallic selenium by the broad-line NMR method.[3] In the present study we obtained and investigated, probably for the first time, high-resolution NMR spectra of ^{77}Se nuclei in a solid–single-crystal selenious acid H_2SeO_3.

Selenious acid has a rhombic structure with four molecules per unit cell ($a=9.132$ Å, $b=5.988$ Å, $c=5.091$ Å).[4] The space group is $P2_12_12_1$. The SeO_3 group is bound in the crystal by four different hydrogen bonds and is greatly distorted. In accordance with the crystal symmetry, in the general case the NMR spectrum of ^{77}Se should consist of four lines, and in the case of rotation about the axes *a*, *b*, and *c* it should consist of two lines that merge into one when the magnetic field is directed along one of these axes.

The selenious-acid single crystals were grown from a saturated aqueous solution. The crystals were oriented with the aid of an x-ray diffractometer. To record the NMR spectra we used crystals of 9 mm diameter and 5–10 mm length. The orientational dependence of the CS of the ^{77}Se NMR lines was plotted by rotating the crystals 5° about the crystallographic axes, *a*, *b*, and *c* at room temperature. To decrease the spin-lattice relaxation time T_1, the crystals were irradiated with ^{60}Co source at a dose ~ 5 Mrad. The NMR spectra of ^{77}Se were recorded with a laboratory-built broadband pulsed double-resonance spectrometer in a field 14.09 kOe. The magnetic field of the RF pulse for the protons was 8 Oe and was sufficient to suppress the ^1H–^{77}Se dipole-dipole interaction. The cross-polarization time was 4 msec. The width of an individual ^{77}Se NMR line was 80 Hz. The reference was concentrated selenic acid H_2SeO_4.

The orientational dependences of the CS of the ^{77}Se nuclei are shown in Fig. 1. As expected, the NMR of the selenium nuclei, in the case of rotation around the crystallographic axes, consist of two lines, and when account is taken of the crystal symmetry

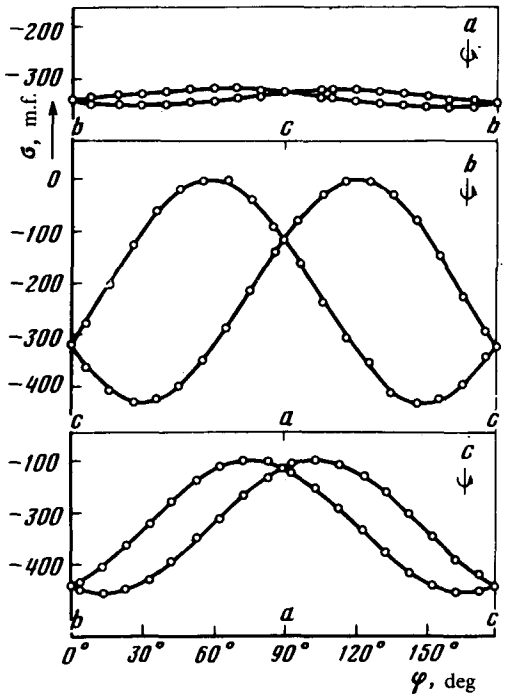

FIG. 1. Orientational dependences of the positions of the ^{77}Se NMR lines in a selenious-acid crystal, with rotation about the three crystallographic axes. The chemical shift is indicated relative to liquid selenic acid H_2SeO_4.

they correspond to one structurally nonequivalent SeO_3 group. Analysis of the experimental orientational dependences of the CS was carried out by a standard procedure,[3,5] and the CS tensor was diagonalized with the aid of a computer. The obtained principal values of the screening tensor and their direction cosines are listed in Table I.

In view of the small width of the spectral lines, the experimental error is small and amounts of ± 2 m.f. for the principal values of the tensor and 1° for their orientations. The CS of a 30% aqueous solution of H_2SeO_3 is -270 ± 4 m.f., which is quite close to the isotropic mean value $\bar{\sigma}$ of the obtained tensor. We note that Table I lists

TABLE I. Cs tensor of ^{77}Se nuclei in selenious-acid crystal.

Principal components of the tensor (in m.f.) relative to liquid H_2SeO_4		Direction cosines relative to the crystallographic axes	
σ_{11}	- 450	0.506	0.357	0.785
σ_{22}	- 333	- 0.075	0.925	- 0.372
σ_{33}	1	0.859	- 0.129	- 0.495
$\bar{\sigma}$	-261	—	—	—

the principal values of the components of the CS tensor connected with one of the four SeO_3 groups in the unit cell. In accordance with the symmetry of the crystal, on the basis of only the angular dependence of the NMR spectrum it is impossible to ascribe the obtained tensor to any particular SeO_3 group. There are four different variants of the orientation of the principal axes of the CS tensor of ^{77}Se relative to each SeO_3 group. Inasmuch as none of the variants the directions of the principal axes agree well with the directions of the bonds in the SeO_3 group or with other preferred directions, the final choice calls for additional theoretical investigations of the screening of ^{77}Se in selenious acid, as well as for experimental data on the magnetic screening in other crystals with different symmetry (preferably triclinic), containing SeO_3 groups.

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