Temperature Dependence of the Nuclear Quadrupole Frequencies of ^{23}Na and ^{187}Re in NaReO$_4$

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The temperature dependence of the quadrupole frequency of ^{187}Re measured by NQR and of ^{23}Na measured by NMR has been determined for temperatures between 170 K and 300 K in NaReO$_4$. For both nuclei the quadrupole frequency decreases with increasing temperature. The dependence is stronger for ^{187}Re than for ^{23}Na.

Introduction

The quadrupole coupling constants in solids usually depend on temperature (see f.e. Ref. [1–8]). This can be explained by the change of vibration amplitudes of molecules, but the influence of the volume expansion on the electric field gradient has also to be taken into account [4].

For ^{185}Re and ^{187}Re in some perrhenates NQR measurements have been reported [9–16]. With the exception of NH$_4$ReO$_4$ the NQR signals of ^{185}Re and ^{187}Re in perrhenates yield decreasing quadrupole coupling constants, if the temperature of the solid sample is increased. This is the normal behaviour [9, 11–14, 16], whereas for NH$_4$ReO$_4$ in the temperature range from 100 K to 300 K an inverse effect has been found [11, 12, 16].

To clear this peculiarity of the perrhenates a series of different measurements have been reported: The pressure coefficients of the quadrupole resonance frequencies in perrhenates at various temperatures [15, 16] and also lattice parameters [16, 17] have been determined. Recently some NMR measurements of proton relaxation rates have been published for NH$_4$ReO$_4$ [18–20]. It seems, that the anomalous temperature dependence of the ^{187}Re NQR signal in NH$_4$ReO$_4$ can be explained by reorientation of the ammonium ion and by rearrangement of the lattice [17]. For NaReO$_4$ and KReO$_4$ a detailed study of the temperature dependence of the NQR signal of ^{187}Re has also been reported [13]. Neglecting effects of volume expansion Johnson and Rogers [13] calculated the quadrupole frequency of ^{187}Re as a function of temperature. They realized that the change in the field gradient with expansion of the lattice is important and cannot be neglected.

The field gradients at the sodium nuclei in NaReO$_4$ result from the crystalline fields of the Na$^+$ ions and ReO$_4^-$ ions, whereas the field gradients at the rhenium nuclei result partly from the crystalline field and partly from the covalent bonding of the distorted perrhenate tetrahedron [9]. Therefore the change of the ^{23}Na quadrupole coupling constant with temperature may give valuable information of the quadrupole interaction of the rhenium nuclei. According to this fact we have measured the temperature dependence of the quadrupole coupling constant of ^{187}Re and of ^{23}Na in NaReO$_4$ by observing NQR signals of ^{187}Re and NMR signals of ^{23}Na.

Experimental

Measurements of the quadrupole coupling constant of the nuclei ^{185}Re, ^{187}Re and ^{23}Na were performed on the same spectrometer, a multinuclei Bruker pulse spectrometer SXP 4-100. The NQR and NMR free induction decays were digitized by the Bruker transistore BC-104, which has a fast analog-to-digital-converter, accumulated and Fouriertransformed by the Bruker B-NC 12 data unit.

For ^{23}Na the quadrupole splitted NMR signal was investigated in a magnetic field of 2.114 T at 23.81 MHz, whereas for ^{185}Re at 89.99 MHz and 44.99 MHz and for ^{187}Re at 85.18 MHz and 42.58 MHz pure quadrupole frequencies have been observed for the $(\pm 5/2, \pm 3/2)$ and $(\pm 3/2, \pm 1/2)$ transitions at 298 K. For all measurements a cylindrical sample with 10 mm outer diameter and about 1 cm^3 sample volume has been used.

For ^{23}Na a signal-to-noise ratio of about 60 could be achieved within 40 minutes of measuring time and for the $(\pm 3/2, \pm 1/2)$ transition of ^{187}Re a signal-to-noise ratio of about 35 within 0.5 minutes.

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The temperature was stabilized by the Bruker temperature controller B-ST 100/700.

NaReO$_4$ has the Scheelite (CaWO$_4$) structure, the space group is I4$_1$, with both the anions and cations occupying S$_4$ sites in the crystal [13]. There are 4 molecules per unit cell with the dimensions: $a = 0.5362$ nm and $c = 1.1718$ nm [21]. We used a NaReO$_4$ sample, a gift of Degussa, Hanau, without further purification.

Results and Discussion

For ^{185}Re and ^{187}Re the NQR signals of the $(\pm 5/2, \pm 3/2)$ and $(\pm 3/2, \pm 1/2)$ transitions have been observed at 298 K. But only for the $(\pm 3/2, \pm 1/2)$ transition of ^{187}Re, which yields the strongest signal, the NQR frequency between 200 K and 300 K has been determined. In this temperature range a linear dependence is found (see Figure 1). Using the value of the quadrupole frequency $\nu_Q = 3e^2qQ/(2I(2I-1)h)$, which was measured at 298 K for ^{187}Re and the slope $(\Delta\nu_Q/\Delta T)_p$ (Re) of Fig. 1, which was determined at constant atmospheric pressure one gets:

$$\frac{1}{\nu_Q}\left(\frac{\Delta\nu_Q}{\Delta T}\right)_p \text{(Re)} = (-429 \pm 10) \cdot 10^{-6}\,\text{K}^{-1}\,.$$

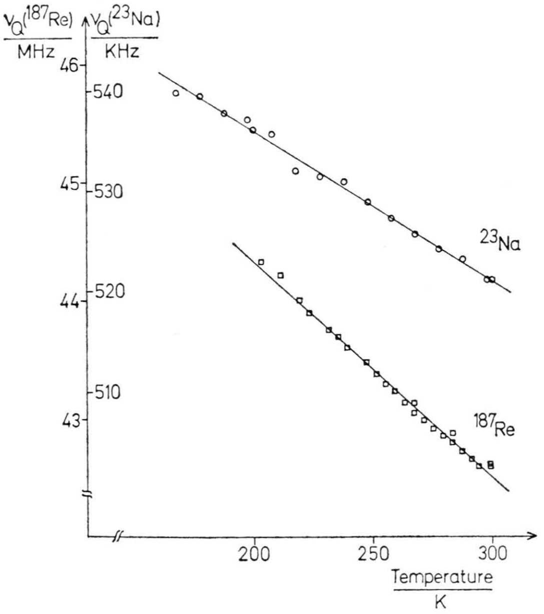

Fig. 1. Temperature dependence of the quadrupole frequency of ^{187}Re measured by NQR for the $(\pm 3/2, \pm 1/2)$ transition and of ^{23}Na measured by NMR at 23.81 MHz in powdered NaReO$_4$.

This temperature dependence of ^{187}Re in NaReO$_4$ is in good agreement with the experimental results of Reference [13]. For two different models, however, temperature dependences of the NMR signal of ^{187}Re in NaReO$_4$ have been calculated in Ref. [13] under the assumption, that no volume expansion occurs for increasing temperature.

With model A

$$\frac{1}{\nu_Q}\left(\frac{\Delta\nu_Q}{\Delta T}\right)_V \text{(Re)} = -84 \cdot 10^{-6}\,\text{K}^{-1}$$

and with model B

$$\frac{1}{\nu_Q}\left(\frac{\Delta\nu_Q}{\Delta T}\right)_V \text{(Re)} = -100 \cdot 10^{-6}\,\text{K}^{-1}$$

can be taken from Fig. 2 of Ref. [13] for temperatures from 200 K to 300 K.

It has already been mentioned that the assumption of constant volume is no good approximation for the temperature dependence of the quadrupole frequency of ^{187}Re in solid NaReO$_4$ [13]. Therefore we have observed in a further experiment the ^{23}Na NMR signal in the same NaReO$_4$ sample in a magnetic field of 2.114 T. A first-order and second-order quadrupole splitted NMR signal was found. This is a very seldom case for ^{23}Na in solids (see e.g. Ref. [22]). From this fact useful information for ν_Q and the asymmetry parameter η can be taken. Because ^{23}Na has a spin of 3/2 the first-order quadrupole splitted signal consists of a central signal and two additional signals, which can be measured relative to the central signal with good accuracy. The frequency separation is equal to $\nu_Q/2 = 3e^2qQ/(4I(2I-1)h)$, if in a powder sample only the divergences of the powder spectrum of the satellites can be observed and if the asymmetry of the electric field gradient tensor vanishes [23]. From the second-order quadrupole splitting of the central line the asymmetry parameter of the electric field gradient tensor can be determined by a computer fit program (see f.e. [24]) to $\eta = (0.0 \pm 0.1)$. The second-order quadrupole splitting of the central signal indicates that no remarkable change of the asymmetry parameter of the electric field gradient at the ^{23}Na nuclei in NaReO$_4$ occurs for temperatures between 170 K and 300 K. In Fig. 1 the measured values of ν_Q for ^{23}Na in NaReO$_4$ versus temperature are also given. Again a linear dependence between 170 K and 300 K is found. In analogy to ^{187}Re for ^{23}Na the following expression can be evaluated:

$$\frac{1}{\nu_Q}\left(\frac{\Delta\nu_Q}{\Delta T}\right)_p (\text{Na}) = (-288 \pm 15)\cdot 10^{-6}\,\text{K}^{-1}.$$

As expected from theoretical reasons as well for ^{187}Re as for ^{23}Na a decrease of the quadrupole frequencies is experimentally found if the temperature is increased. The influence of temperature is stronger for ^{187}Re than for ^{23}Na. But taking into account the theoretical value of the temperature dependence, which has been calculated by Johnson and Rogers [13] for ^{187}Re without volume expansion of the NaReO$_4$ specimen, the experimental temperature dependence of ^{23}Na and ^{187}Re is reasonable.

Because no expansion and compression coefficients have been determined for NaReO$_4$, as far as we know, no further separation of the different contributions to the temperature behaviour of the quadrupole frequencies can be performed.

There are some other examples, for which quadrupole coupling constants have been determined at different temperatures in anions and cations, f.e. NaClO$_3$ and NaBrO$_3$ [25–30]. For these specimens the temperature dependence of Na is stronger than that one of Cl or Br. This may be due to the fact, that the electric field gradient at the Cl or Br nuclei is dominated by the covalent bonding in the anions and hence effects of volume expansion might be less important than for Re in ReO$_4^-$.

The possibility of measuring the quadrupole coupling constants in NaReO$_4$ of both the anions and the cations gives further insight into the mechanism of temperature dependence which will be more obvious if further data on expansion and compression coefficients are available.

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