^{81}Br and ^{127}I NQR of Rare Earth Trihalogenides REX$_3$, X = Br, I*

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The ^{81}Br NQR spectra of REBr$_3$, RE = Dy, Ho, Yb, Sm, and the ^{127}I NQR spectra of REI$_3$, RE = Dy, Ho, Sm, are reported. Additionally ^{127}I NQR data of RbHoI$_4$, KSmI$_4$, and Rb$_3$Sm$_2$I$_9$ are given. The line shape of the ^{127}I NQR of HoI$_3$ was studied in external magnetic fields up to 300 Gauss.

Introduction

Trihalogenides of rare earth elements show some differences in their crystal lattices. The chlorides and bromides of the light rare earth elements LaCl$_3$...GdCl$_3$; LaBr$_3$...PrBr$_3$, are isomorphous to UCl$_3$ [1]. The trichlorides of the heavy rare earth elements are isomorphous to AlCl$_3$ and the corresponding tribromides crystallize with the FeCl$_3$ type structure [2, 3]. Several tribromides REBr$_3$ (RE = Nd, Eu, Sm, Tb) and the iodides REI$_3$ (RE = La, Ce, Pr, Nd) are isomorphous to PuBr$_3$, whereas the majority of the REI$_3$ shows the BiI$_3$ type structure [4, 5].

NQR is quite a sensitive method with respect to details in the structure of the electrons surrounding the resonating nuclei, and changes in the crystal structure can easily be detected.

Results and Discussion

We have studied several tribromides and triiodides of rare earth elements, and a few compounds formed by rare earth triiodides and alkali iodides. In Table 1 the ^{81}Br and ^{127}I NQR frequencies are listed for $T = 77$ K (in a few cases for 290 K, too).

Since the compounds DyBr$_3$, HoBr$_3$, and YbBr$_3$, are isomorphous to FeCl$_3$ ($C_{3i}^2 - R\bar{3}$, $Z = 6$), a single line ^{81}Br NQR spectrum is expected and the experimental results are in accordance with this expectation (see Table 1). $\nu(^{81}\mathrm{Br})$ increases with decreasing distance M–Br ($d(\mathrm{Dy-Br}) = 2.836$ Å; $d(\mathrm{Ho-Br}) = 2.825$ Å); $d(\mathrm{Yb-Br}) = 2.798$ Å). A small electric field gradient, EFG, is expected at the site of the rare earth ion since RE is surrounded by 6 Br-atoms in almost regular octahedral coordination.

SmBr$_3$ crystallizes in the orthorhombic system (D_{2h}^{17}-Ccmm, $Z = 4$) [3] and the Br-atoms occupy the point positions 4 c and 8 f.

The ^{81}Br NQR spectrum is in agreement with the conclusion which follows from the crystal structure. Two ^{81}Br lines are found, the higher frequency line corresponding to the Br atoms at 4 c; the lower frequency line (position 8 f) shows double intensity.

Sometimes ago Parks and Moulton [6] studied NdBr$_3$ by NQR. They observed two resonance frequencies for ^{81}Br and determined the asymmetry parameter of both EFG tensors. At the side 4 c they found $\eta = 6.8\%$ and at the site 8 f $\eta = 48.7\%$.

The rare earth triiodides studied by us have the BiI$_3$ type structure. As can be seen from Table 1, the asymmetry parameter of the EFG at the iodine site

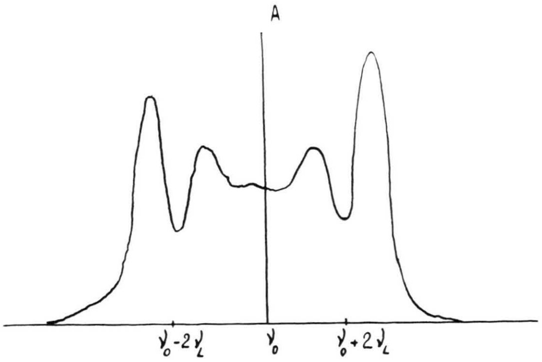

Fig. 1. The line form of NQR ^{127}I ($\Delta m = 3/2 - 5/2$) in the polycrystalline sample of HoI$_3$ located in the external magnetic field $3 \cdot 10^{-2}$ T. ν_L = Larmor frequency.

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Table 1. NQR frequencies of ^{81}Br and ^{127}I, quadrupole coupling constants, $e^2 \Phi_{zz} Q h^{-1}$ (^{127}I), and asymmetry parameters η(^{127}I), in some trihalogenides of the rare earth elements. ν(^{81}Br) at $T = 77$ K.

Substance	ν (^{81}Br)/MHz
$DyBr_3$	30.36
$HoBr_3$	31.194
$YbBr_3$	34.224
$SmBr_3$	24.985
	46.665

Substance	ν (^{127}I)/MHz, $\Delta m = 1/2-3/2$	ν (^{127}I)/MHz, $\Delta m = 3/2-5/2$	$e^2 \Phi_{zz} Q h^{-1}$ / MHz	η (%)	T/K
DyI_3	42.15	83.33	276.7	9.5	77
	42.24	82.80	278.3	13.5	290
HoI_3	43.46	85.84	286.7	10.0	77
	43.50	85.23	286.8	14.0	290
SmI_3	36.72	72.76	242.5	9.0	300
$RbI \cdot HoI_3$	38.19	74.30	248.2	15.0	77
$KI \cdot SmI_3$	41.09	80.64	270.3	12.5	77
$3RbI \cdot 2SmI_3$	34.01	63.29	214.4	24.0	77
	46.49	86.94	294.1	23.0	

is rather small ($\approx$ 10%). This points out that there is a small deviation of the iodine positions from the ideal BiI_3 type structure in which the point symmetry of the iodine would be 3 ($\eta \equiv 0$).

For SmI_3 the ^{127}I NQR frequency ($1/2 \rightleftharpoons 3/2$) was found to increase very little with decreasing temperature ($\sim$ 0.012 kHz/degree). In the range $110 \leqq T/\mathrm{K} \leqq 120$ the intensity of the line becomes very weak and at $T = 77$ K no ^{127}I NQR signal was detected in the range $50 \leqq \nu/\mathrm{MHz} \leqq 150$.

HoI_3 shows a very strong transition $3/2 \rightleftharpoons 5/2$ and the signal to noise ratio is 100 on the oscilloscope. The ^{127}I Zeeman spectrum on polycrystalline material was studied at 77 K in a field $B_0 = 3 \cdot 10^{-2}$ T ($B_0 \parallel B_{\mathrm{HF}}$). It was found that the shape of the band is very similar to that found for Sb in Sb_2O_3 and Re in $NaReO_4$ [7], but different from the shape expected in case of negligible dipole-dipole interactions. This effect can be observed by comparing the ^{35}Cl Zeeman NQR powder spectrum of $NaClO_3$ and $KClO_3$, where in the latter compound dipolar interactions are very small.

The ^{127}I NQR Zeeman powder spectrum ($3/2 \rightleftharpoons 5/2$) of SmI_3 is shown in Figure 1. It seems to be of interest to elaborate the theory of NQR line shape by incorporating dipole-dipole interactions.

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