Nuclear Quadrupole Resonance of Antimony in $Ln_3Sb_5O_{12}$ Crystals

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Complete ^{121,123}Sb NQR spectra of crystalline rate earth antimonites $Ln_3Sb_5O_{12}$ (Ln = La, Nd, Er, Lu) were recorded at 77 K. The quadrupole coupling constants and asymmetry parameters of the electric field gradient were measured. A "lanthanide compression" effect on the antimony NQR was observed. Using relations found for the antimonites under study, the Sb spectral parameters of other lanthanide compounds can be predicted.

Key words: NQR, Rare earth antimonites, ^{121,123}Sb, "Lanthanide compression".

1. Introduction

Antimonite crystals of the general formula $Ln_3Sb_5O_{12}$ (Ln = La–Lu) are nonlinear optic materials with more or less pronounced ferroelectric characteristics. New information on the interatomic interactions in these compounds is desirable.

In this paper ^{121,123}Sb NQR spectra of such crystals with Ln = La, Nd, Er, Lu were studied at 77 K.

According to an X-ray structure analysis (XRSA), $Ln_3Sb_5O_{12}$ crystallize in space group $\bar{I}43m$ with $Z = 4$ [1]. There are two crystallographically nonequivalent antimony atoms in the structure. The coordination number of the antimony atom in position A (site symmetry 3m) is 3, that of the antimony atom in position B (site symmetry mm) is 4. If one takes into account the electron lone pair of the antimony atoms, the coordination polyhedron of the Sb (A) atom will be a distorted tetrahedron with a pronounced threefold axis; the coordination polyhedron of the Sb (B) atom will be a distorted trigonal bipyramid [1]. All $Ln_3Sb_5O_{12}$ crystals are isomorphous and differ only in their unit cell volumes (see Table 5.6, p. 243 in [1]).

2. Experimental

The ^{121,123}Sb NQR spectrum at 77 K was known previously for praseodymium antimonite $Pr_3Sb_5O_{12}$ [2]. We refined the spectrum and, additionally, measured the antimony NQR spectra in lanthanum, neodymium, erbium and lutetium antimonites.

All measurements were made at liquid nitrogen temperature on the pulse NQR spectrometer ISSh-2-13. Errors in measuring the spectral line centers did not exceed 8 kHz.

Complete NQR spectra of both antimony isotopes in the compounds under study are listed in Table 1. The NQR spectra of all studied specimens are of the same type and correspond to two crystallographically nonequivalent positions of the antimony atoms. Small values of the quadrupole coupling constants (e^2Qq_{zz}) and the asymmetry parameter (η) of the electric field gradient (EFG) tensor correspond to antimony atoms in position (A); large values of e^2Qq_{zz} and η correspond to antimony atoms in position (B). For Sb (A), changes in e^2Qq_{zz} at 77 K are in the interval 451.695÷485.568 MHz ($\Delta e^2Qq_{zz} = 33.813$ MHz), while η varies from 1.07 to 1.34% ($\Delta\eta = 0.27\%$). For Sb (B), e^2Qq_{zz} varies from 564.100 to 567.982 MHz ($\Delta e^2Qq_{zz} = 3.882$ MHz) and η from 69.15 to 54.70% ($\Delta\eta = 14.45\%$). As is seen, the largest changes for position (A) are associated with e^2Qq_{zz}, i.e. one can consider it as monoaxial, since changes in η are small. On the contrary, for position (B) changes mainly occur in the transverse components of the EFG tensor, eq_{xx} and eq_{yy}, since $\eta = |(q_{xx}-q_{yy})/q_{zz}|$.

3. Results and Discussion

For the lanthanide-containing compounds, effects associated with the so called "lanthanide compres-

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Table 1. ^{121,123}Sb NQR spectra of $Ln_3Sb_5O_{12}$ compounds at 77 K.

Ln	Position of Sb atom	Sb isotope	ν_1 [a] MHz	ν_2 MHz	ν_3 MHz	e^2Qq_{zz} MHz	η %
La	A	121	67.760	135.510	–	451.695	1.07
		123	41.150	82.250	123.380	575.798	
	B	121	120.506	157.050	–	564.100	69.15
		123	105.200	93.335	146.280	719.086	
Pr	A	121	68.82	137.64	–	458.807	1.19
		123	41.78	83.51	125.36	584.864	
	B	121	116.28	157.35	–	561.381	65.03
		123	100.20	93.07	146.67	715.620	
Nd	A	121	69.246	138.466	–	461.567	1.22
		123	42.050	84.048	126.080	588.383	
	B	121	116.730	158.310	–	564.384	64.67
		123	100.490	93.520	147.350	719.449	
Er	A	121	71.985	143.939	–	479.814	1.28
		123	43.715	87.370	131.064	611.643	
	B	121	111.180	161.210	–	567.664	57.11
		123	93.000	94.640	149.760	723.629	
Lu	A	121	72.850	145.666	–	485.572	1.34
		123	44.242	88.417	132.637	618.983	
	B	121	109.356	161.900	–	567.983	54.70
		123	90.490	94.976	150.319	724.036	

[a] ν_1, ν_2, ν_3 frequencies of transitions (1/2−3/2), (3/2−5/2), (5/2−7/2), respectively.

sion" are well known. Therefore, an attempt was made to determine the effect of that phenomenon on the quadrupole coupling constant changes for both positions of antimony atoms. If for the La-specimen the quadrupole coupling constant is $e^2Qq_{zz}(\mathrm{La}) \sim (1/r_0)^3$, then for the other lanthanides $e^2Qq_{zz}(\mathrm{Ln}) \sim [1/(r_0 + \Delta r_n)]^3$. Then

$$\frac{e^2Qq_{zz}(\mathrm{La})}{e^2Qq_{zz}(\mathrm{Ln})} = (1 + \Delta r_n/r_0)^3 . \tag{1}$$

Hence

$$\frac{\Delta r_n}{r_0} = \left[\frac{e^2Qq_{zz}(\mathrm{La})}{e^2Qq_{zz}(\mathrm{Ln})}\right]^{1/3} - 1 . \tag{2}$$

The $\Delta r_n/r_0$ ratio (in %) and the number of f-electrons (N_f) in the f-subshell of the lanthanide atom are related.

For position (A) the relation is linear:

$$\Delta r_n/r_0 = -0.1765 \cdot (0.105 + N_f) \pm 0.02\%; \quad n = 5, \quad r = 0.9997 . \tag{3}$$

Table 2. Electronic and geometric characteristics of $Ln_3Sb_5O_{12}$ crystals.

Ln	N_f	$r(Ln^{3+})$ [3] Å	V [2] Å^3	$(\Delta r_n/r_0)_A$ %	$(\Delta r_n/r_0)_B$ %
La	0	1.06	1382	0	0
Pr	3	1.01	1341	−0.5201	0.1612
Nd	4	1.00	1323	−0.7188	−0.0165
Er	12	0.88	1235	−1.9936	−0.2097
Lu	14	0.85	1207	−2.3823	−0.2284

The $\Delta r_n/r_0$ values for position (A) can also be compared (see Table 2) with relative changes in the size of the Ln^{3+} ions, $\delta r = [r(Ln^{3+}) - r(La^{3+})]/r(La^{3+})$:

$$\Delta r_n/r_0 = (0.0021 + 0.1193\,\delta r) \pm 0.03\%; \quad n = 5, \quad r = 0.9994, \tag{4}$$

or

$$\delta r \approx 8.39(\Delta r_n/r_0) \pm 0.15\% . \tag{4'}$$

It is interesting to note that in the crystals under study a linear dependence between $e^2Qq_{zz}(\mathrm{A})$ and the inverse volume of the unit cell (V^{-1}) is observed:

$$e^2Qq_{zz}(\mathrm{A}) = 215.912 \cdot (1 + 1508\ V^{-1}) \pm 0.22; \quad n = 5, \quad r = 0.9997 , \tag{5}$$

which fairly well corresponds with results obtained in [3, 4].

Equation (5) is likely to allow to predict the QCC values for $Ln_3Sb_5O_{12}$ crystals, the cell volumes and Ln^{3+} ion sizes of which are known (see Table 2 and [1, 5]).

As for position (B), where the perturbation caused by the lanthanide atom mainly affects the transverse EFG components eq_{xx} and eq_{yy}, one should expect $\Delta r_n/r_0 = F(N_f)$ to be a quadratic equation. Actually, the relation is described by a shifted hyperbola

$$\left[\frac{(\Delta r_n/r_0 - a_0)}{\Delta r}\right]^2 - \left[\frac{(N_f - b_0)}{\Delta N}\right]^2 = \delta , \tag{6}$$

where $a_0 = 0.0668\%$, $\Delta r = 0.0915\%$, $b_0 = 3.7568$, $\Delta N = 3.034$ and $\delta = \pm 1$. The correlation coefficient between $(\Delta r_n/r_0)$ values calculated using (6) and (2) is 0.999.

The graphical solution of equations (3) and (6) is represented in Figure 1. Thus, as follows from (3) and (6), changes in the quadrupole coupling constants are mainly due to changes in the lanthanide atom size, provided the general structural pattern remains the same.

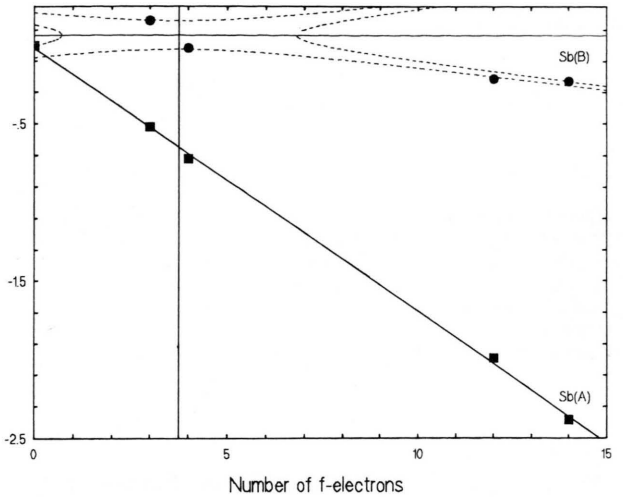

Fig. 1. Graphical solution of (3) and (6). The ordinate shows $\Delta r_n/r_0$ for position (A) and for position (B).

A dependence between e^2Qq_{zz} and η in the series of analogous compounds was shown to exist in [6]:

$$e^2Qq_{zz} = e^2Qq_0 + \frac{B\delta}{2\Delta\eta} \ln \left| \frac{\eta - (\eta_0 + \Delta\eta)}{\eta - (\eta_0 - \Delta\eta)} \right|, \quad (7)$$

Table 3. Parameters of (7) for Sb atoms in $Ln_3Sb_5O_{12}$ compounds.

Position of Sb atom	e^2Qq_0 MHz	B MHz · %	η_0 %	$\Delta\eta$ %	$\delta(e^2Qq_{zz})$ MHz	r
A	454.878	0.9014	1.380	0.089	0.61	0.998
B	563.191	29.989	46.113	9.398	0.23	0.997

where e^2Qq_0 and η_0 is the origin, B and $\Delta\eta$ are constants, $\delta = \pm 1$. Relevant parameters of (7) for both antimony positions are listed in Table 3.

4. Conclusions

As follows from an analysis of spectral and structural data for the whole $Ln_3Sb_5O_{12}$ series, one might estimate expected values of the quadrupole coupling constants and asymmetry parameters of the EFG tensor. In this case (1), (2), and (3) are used for the antimony atoms in position (B). Values of η can be determined from (7) and Tables 1 and 3.

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