

ELECTRON SPIN RESONANCE OF Gd^{3+} IN CERAMIC $PbTiO_3$

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ABSTRACT

The electron spin resonance spectra of Gd^{3+} in ceramic $PbTiO_3$ and, as a comparison, in powdered $Bi_3Mg_2(NO_3)_{12} \cdot 24H_2O$ are reported. The interpretation, in terms of crystal field parameters, of the spectrum of the double nitrate is in good agreement with previous single crystal results. It was not possible to interpret the room temperature spectrum of $PbTiO_3$. However, the spectrum of this compound measured above its Curie-temperature (~ 763 K) can be interpreted. This shows that the local crystal field symmetry of a small part of the Gd^{3+} -ions at this temperature is orthorhombic or lower, notwithstanding the cubic lattice symmetry of $PbTiO_3$ under these conditions.

Introduction

The work reported here forms part of a more extensive research effort directed at studying the structure and properties of ceramic rare earth substituted lead titanate and zirconate compounds (1,2,3,4,5). These are of interest because of their ferro- and piezo-electric behaviour. The usual methods of structure determination, such as X-ray diffraction, only give an overall picture of the structure. In the interpretation of the properties it is desirable to obtain a more complete insight into the detailed, local structure. For this purpose the spectra of tracer ions can be used (6,7). In this case a small amount of Gd^{3+} was built into $PbTiO_3$ and its electron spin resonance spectrum measured.

The spin Hamiltonian for this ion, which has an $^8S_{7/2}$ ground state, can be written as (8):

$$\hat{H} = g\beta\vec{H} \cdot \hat{S} + \frac{1}{3} \sum_{m=-2}^2 b_2^m \hat{O}_2^m + \frac{1}{60} \sum_{m=-4}^4 b_4^m \hat{O}_4^m + \frac{1}{1260} \sum_{m=-6}^6 b_6^m \hat{O}_6^m \quad (1)$$

with: \vec{H} = magnetic field; \hat{S} = spin operator; \hat{O}_n^m = equivalent

spin operator; $b^m =$ crystal field parameter.

The crystal field does not split an S-state to first order so that g is isotropic.

Most of the work published on the electron spin resonance of Gd^{3+} has been concerned with single crystals, for a review see (7). Reynolds et.al. (9) have also studied powdered compounds with the orthorhombic $ZrSiO_4$ structure and used the results in the interpretation of single crystal spectra.

To achieve a better insight into the interpretation of the e.s.r. spectra of powdered compounds, $(Bi_{0.99}Gd_{0.01})_2Mg_3(NO_3)_{12} \cdot 24H_2O$ was studied for comparison purposes.

Experimental

The double nitrate was synthesized according to the method of Gerkin and Thorsell (10). Analysis of the product showed its composition to be in close agreement with the formula given above.

$PbTiO_3$ was synthesized using two different methods. In the first a solid state reaction between the pure oxides was used (2). The second was based upon the so-called citrate method (11). The lead titanate powders were heat-treated for some hours at 1100 to 1200°C and subsequently powdered. X-ray diffraction showed no traces of other compounds and the line widths indicated that they were homogeneous. X-ray fluorescence analysis showed the composition of all samples to be in close agreement with the composition given above.

Electron spin resonance measurements were performed around 9.5 GHz, at room temperature with a Varian E-12 spectrometer and at high temperatures with a Varian E-15 spectrometer using a high-temperature cavity developed by Koningsberger (12).

Interpretation of Gd^{3+} -powder e.s.r. spectra

When the magnetic field direction is parallel to the principal crystal field axis (denoted the z-axis) in the case of an axial crystal field seven transitions are possible. These occur between states for which the $M_S = +7/2, \dots, -7/2$ are good quantum numbers. The transition $+7/2 \rightarrow +5/2$ occurs at the lowest, $-5/2 \rightarrow -7/2$ at the highest magnetic field.

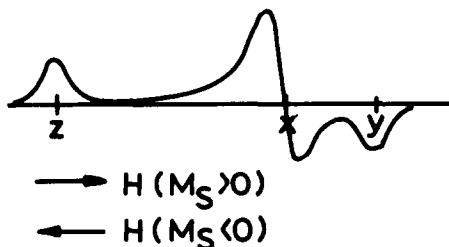


FIG. 1

Schematic form of derivative of e.s.r. absorption band for powdered samples for transition $M_S \rightarrow M_S - 1$ ($M_S \neq \frac{1}{2}$), where x, y and z are the principal crystal field axes resonances.

When the field does not coincide with the crystal field axis, mixing of the different states occurs and the M_S are no longer good quantum numbers. In a powder spectrum this leads to an absorption band of which the derivative form is sketched in figure 1. The magnetic fields at which resonances appear in the derivative spectrum experimentally obtained, correspond to the resonance fields for a single crystal when measured along its principal axes.

For the total spectrum this gives the final result that the ($z, 7/2 \rightarrow 5/2$) transition lies at the lowest and the ($z, -5/2 \rightarrow -7/2$) transition at the highest magnetic field.

Reynolds, et al. (9) have shown that with orthorhombic crystal field symmetry, when higher order quadratic terms are omitted, the following relation applies to the magnetic fields at which these transitions occur:

$$H_{(z, \frac{7}{2} \rightarrow \frac{5}{2})} - H_{(z, -\frac{5}{2} \rightarrow -\frac{7}{2})} = \frac{12b_2^0 + 40b_4^0 + 12b_6^0}{g\beta} \quad (2)$$

where $H(i, M_S \rightarrow M_S - 1)$ is the field value at which a transition corresponding with the direction i , occurs. In most cases $b_2^0 \gg b_4^0, b_6^0$. This makes it possible to obtain a first estimate of b_2^0 from equation (2). Similar relations exist (9) for the other transitions. Thus successively better estimates of the crystal field parameters are obtained by trial and error.

In principle a further splitting or shift of the lines is

TABLE I
Nuclear Properties of Gd-isotopes.

Species	Abundance %	Nuclear spin	Hyperfine splitting constant (Gauss)	Quadrupole moment
Gd ¹⁵⁵	15	3/2	4-5	1.1
Gd ¹⁵⁷	15	3/2	~ 6	1.0

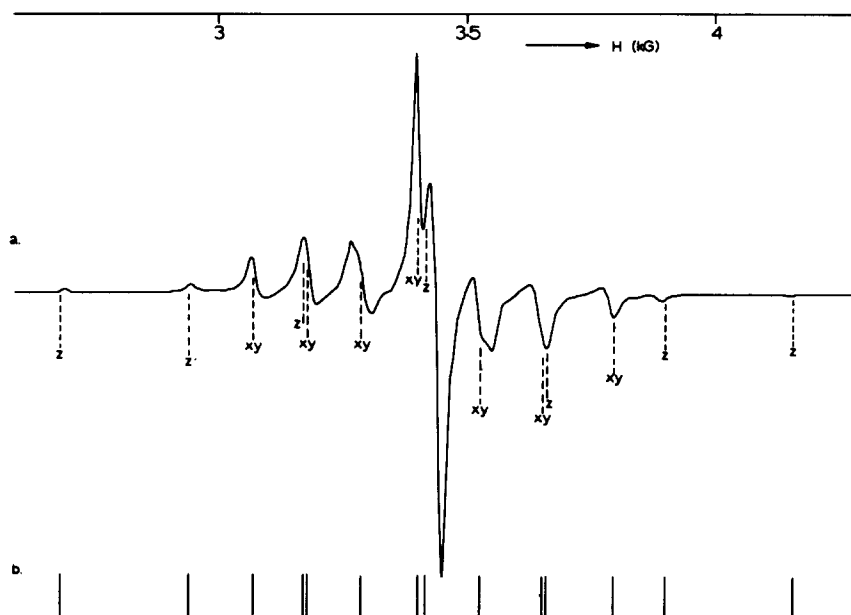


FIG. 2

- a. E.s.r. spectrum of powdered $(\text{Bi}_{0.99}\text{Gd}_{0.01})_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ at roomtemperature ($\nu = 9528.3$ MHz).
- b. E.s.r. line positions along the principal axes calculated from parameters, as derived from the powder spectrum, given in column 2 of table II.

caused by nuclear hyperfine and quadrupole effects. For gadolinium the appropriate parameters are given in table I. Both effects, however, are small with respect to the experimental linewidths in our spectra (30-50 Gauss) so that their influence can be neglected. This supports the use of the simplified spin Hamiltonian of equation (1).

Results and discussion

The observed electron spin resonance spectrum of the bismuth magnesium double nitrate, obtained at room temperature, is shown in figure 2a. With the above mentioned method the set of crystal field parameters given in column 2 of table II, is derived. With these parameters the resonance fields were calculated by means of a direct diagonalization of the energy matrix obtained with the spin Hamiltonian (1). Which gives the line spectrum of figure 2b. In table II a comparison is also shown with the only available single crystal results, obtained in 1953 by Trenam (13). As the method of calculation is based on orthorhombic symmetry the parameters b_4^3 , b_6^3 and b_6^6 , which would be expected to be different from zero as a consequence of the actual symmetry, are not found.

TABLE II

Crystal Field Parameters and g-values for $(\text{Bi}_{0.99}\text{Gd}_{0.01})_2\text{Mg}_3(\text{NO}_3)_{12}\cdot 24\text{H}_2\text{O}$ at Room Temperature.

parameters	from powder spectrum (cm^{-1})	from single crystal a) (cm^{-1})
g	1.991(1) (b)	1.992(2)
b_2^0	$113(1) \times 10^{-4}$	$124(2) \times 10^{-4}$
b_2^2	0(2) "	0
b_4^0	0.2(2) "	0.9(1) "
b_4^4	-2(5) "	0
b_6^0	0.4(2) "	0.6(1) "
b_6^6	-	12(1) "

a) from Trenam (13)

b) Numbers between parentheses are uncertainties in last digit.

In figure 3 the room temperature e.s.r. spectrum of Gd^{3+} in lead titanate is shown. The spectra were found to be independent of the method of synthesis. Interpretation of this spectrum, using the method described above, was found to be impossible.

It is known that the lattice symmetry of lead titanate changes from tetragonal to cubic at the ferroelectric Curie temperature (~ 763 K). It was expected that this change in symmetry would lead to a single line spectrum at high temperatures, which was indeed observed with $g = 1.991 \pm 0.002$. Furthermore, at sufficiently high amplification a number of weak lines appeared superposed on this line, as shown in figure 4. These cannot be explained by nuclear hyperfine or quadrupole splitting as these would cause much smaller splittings as shown by the data of table I. The

large central peak ($\Delta M_S=1$) and the transitions with $\Delta M_S=2, 3$ and 4 (shown in figure 4 at low fields) can be attributed to Gd^{3+} -ions which are situated on non-deformed cubic sites.

Interpretation of the additional spectrum with the method discussed in the previous section is again possible. This gives the crystal field parameters:

$$b_2^0 = (212 \pm 4) \times 10^{-4} \text{ cm}^{-1}, \quad b_2^2 = (120 \pm 20) \times 10^{-4} \text{ cm}^{-1},$$

$$b_4^4 = -(30 \pm 20) \times 10^{-4} \text{ cm}^{-1} \text{ with } g = 1.998 + 0.006.$$

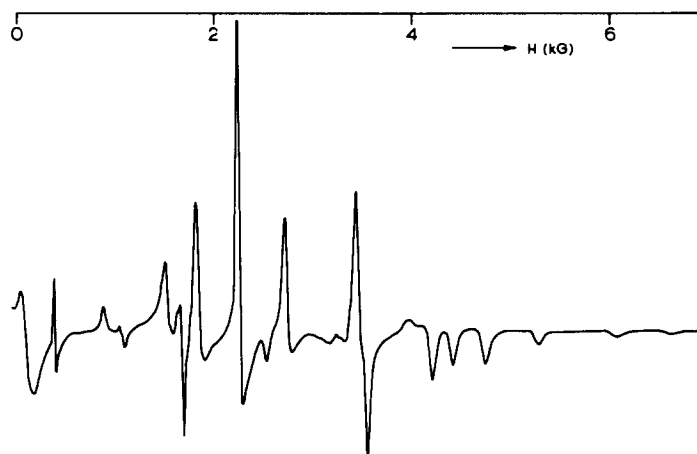


FIG. 3

Electron spin resonance spectrum of $(Pb_{0.9963}Gd_{0.0025})TiO_3$ at 293 K ($\nu = 9153.9$ MHz).

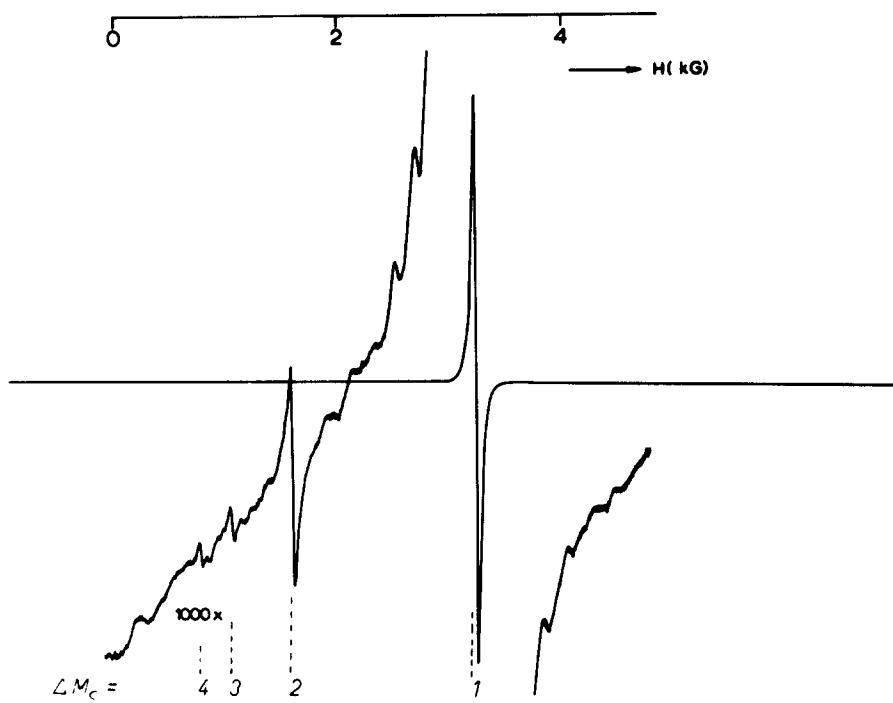


FIG. 4

E.s.r. spectrum of $(Pb_{0.9963}Gd_{0.0025})TiO_3$ at 800 K ($\nu = 9150$ MHz).

The presence of the relatively large b_2^0 and even b_2^2 parameters show that, notwithstanding the cubic lattice symmetry of lead titanate at this temperature, the local field symmetry around some of the Gd^{3+} -ions cannot be cubic or tetragonal but must be orthorhombic or lower. A possible explanation is association of the Gd^{3+} -ion, situated either on a lead or on a titanium site, with lead vacancies in the second coordination sphere.

Work is in progress now to design a computer simulation program, to obtain also a complete set of crystal field parameters from spectra due to a less symmetric crystal field. This will be used in the interpretation of the $PbTiO_3$ spectra obtained at temperatures below the Curie temperature and the spectra of rare earth substituted lead titanates and zirconates.

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