

EPR AND SPIN–LATTICE RELAXATION OF RARE-EARTH ACTIVATED CENTRES IN Y_2SiO_5 SINGLE CRYSTALS

I.N. KURKIN and K.P. CHERNOV

V.I. Ul'yanov-Lenin Kazan State University, Faculty of Physics, USSR

Received 9 May 1979

Revised 12 March 1980

An investigation of the EPR spectra and spin–lattice relaxation of Ce^{3+} , Nd^{3+} , Er^{3+} and Yb^{3+} ions in Y_2SiO_5 single crystals has been carried out. Two different EPR spectra for each rare-earth ion are observed due to a substitution of Y_1 and Y_2 sites in a crystal. Spin–lattice relaxation times for both activated centres are shown to be essentially different, although static crystal fields of Y_1 and Y_2 sites differ slightly.

1. Introduction

The first systematic investigations of Y_2SiO_5 began in 1958 [1]. At present, the formation and crystallization processes [1], physicochemical and electrical characteristics [2] and also the crystal structure of Y_2SiO_5 [3–5] have been studied in detail. As a result of an investigation of the radiation spectrum under cathode excitation of Y_2SiO_5 , activated by rare-earth ions, it was concluded that one might be able to use these crystals as new bases for cathode luminophores [6].

Y_2SiO_5 crystals are of some interest as laser material in as much as, in addition to being very hard, they possess a wide optical band of transparency (0.18–4.9 μm at a sample thickness of 1 mm [7]). Bagdasarov et al. [7] observed pulse-stimulated radiation of a Y_2SiO_5 crystal doped by 2% Nd^{3+} at 300 and 77 K on $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ and $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{13/2}$ transitions. Other investigations on a $\text{Y}_2\text{SiO}_5 + \text{Nd}^{3+}$ system [8] at the same temperature revealed $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ and $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ transitions. There is no data in the literature about electron paramagnetic resonance (EPR) and spin–lattice relaxation (SLR) of rare-earth ions (RE^{3+}) in Y_2SiO_5 . Such information would give an unambiguous answer to the number of activated centres and also yield information on their properties, e.g. the local symmetry of the environ-

ment and the position of the nearest excited Stark level, which could be used for identification of optical spectra. It seems that a lack of these data is a reason for contradictory conclusions about the number of activated centres Nd^{3+} in Y_2SiO_5 in papers [7,8].

In this paper we present the results of an investigation of EPR and SLR of activated centres of Ce^{3+} , Nd^{3+} , Er^{3+} and Yb^{3+} ions in Y_2SiO_5 .

2. Crystal structure of Y_2SiO_5

Y_2SiO_5 single crystals are monoclinic with the $\text{C}_{2h}^6 \equiv \text{I}2/\text{c}(\text{a})$ space group. The parameters of the monoclinic unit cell are as follows: $a = 10.410 (\pm 0.003) \text{ \AA}$, $b = 6.721 (\pm 0.002) \text{ \AA}$, $c = 12.490 (\pm 0.005) \text{ \AA}$, $\beta = 102^\circ 39'$ [5]. A unit cell comprises eight molecules of Y_2SiO_5 . Yttrium atoms occupy two crystallographic sites (Y_1 and Y_2) in distorted octahedrons YO_6 , with a triclinic local symmetry C_1 . Silicon and oxygen ions also occupy sites with the local symmetry C_1 . Fig. 1 shows the Y_2SiO_5 structure in a projection to the ac plane.

The character of the EPR spectra is closely connected with crystal structure properties. Therefore, using the tables from ref. 9 we shall describe below the possible EPR spectra for substitution of param-

Table 1
The EPR data of rare-earth ions in Y_2SiO_5 single crystals

Ion	Centre type	$g_z \equiv g_{\max}$	g_n	$\angle g_z g_n$ (deg.)
Ce^{3+}	I	2.353 ± 0.002	2.25 ± 0.07	(13.5 ± 1)
	II	2.190 ± 0.002	1.15 ± 0.05	(88.5 ± 1)
Nd^{3+}	I	3.825 ± 0.004	3.4 ± 0.2	(32 ± 1)
	II	4.171 ± 0.004	2.46 ± 0.06	(55 ± 2)
Er^{3+}	I	15.465 ± 0.01	9.0 ± 1.5	(57 ± 3)
	II	14.804 ± 0.01	4.5 ± 0.6	(73 ± 3)
Yb^{3+}	I	6.612 ± 0.006	1.6 ± 0.2	(85 ± 2)
	II	6.117 ± 0.006	<0.8	(86 ± 2)

because the magnitude of the magnetic field was not sufficiently high. As a result, the spin hamiltonian parameters were not determined. g -values of EPR lines were obtained by using the usual relation $h\nu = g\beta H$. The maximum g -values ($g_{\max} \equiv g_z$) for each centre are given in table I. The minimum g -values were smaller than 0.8 in all cases. Owing to the strong angular dependence of the intensity of the EPR spectrum it was impossible to determine whether or not one of the centres was more favourable than the others for activation by RE^{3+} ions, except in the case of a Ce^{3+} ion which has a weaker angular dependence than other ions. From the intensity of the EPR lines from each activated centre we can conclude that the probability of Ce_{II} centre activation is approximately one order of magnitude lower than for Ce_I .

Since the local symmetries of Y_1 and Y_2 positions do not differ, the symmetries of the EPR spectra of these centres do not differ either. This is why it is impossible to juxtapose the observed magnetic centres to Y_1 and Y_2 positions in a crystal using the EPR method only. One can only separate the centres related to different Y positions on the basis of some complementary data. For this reason additional measurements were carried out.

All investigated crystals have a poorly marked plane of cleavage. The C_2 axis was experimentally proved to lie in this plane. The direction perpendicular to the plane of cleavage (denoted n) was taken as a control direction when the EPR spectrum was correlated with an activated centre. Both g -factors in the n direction (g_n) for each centre and angles between g_z and g_n ($\angle g_z g_n$) were measured. The results of these

measurements are given in table I. The accuracy of the measurement of g_n is not high owing to the fact that the g -factors have a strong angular dependence and the $H_0 \parallel n$ direction was determined in a mechanical way to an approximation of $\approx 3^\circ$.

A certain tendency in the data is observed in table I. g_n is always considerably greater for one centre than for the other, while the $\angle g_z g_n$ for this centre is smaller than for the other. The centre with greater g_n , and a smaller $\angle g_z g_n$, was labelled as the RE_I^{3+} centre while the other centre was labelled as RE_{II}^{3+} centre. g_z -values for these centres differ little (approximately 10%), and for all ions, except for Nd^{3+} , g_z for the RE_I^{3+} centre is greater than for the RE_{II}^{3+} centre.

This separation of centres is rather conventional. We carried out a spin–lattice relaxation (SLR) investigation of RE^{3+} ions in Y_2SiO_5 in order to obtain additional information about the properties of activated centres.

4. Spin–lattice relaxation of Ce^{3+} , Nd^{3+} , Er^{3+} and Yb^{3+} ions in Y_2SiO_5

A study of the temperature dependences of the SLR times for samples of $Y_2SiO_5 + 0.05\% Ce^{3+}$, $Y_2SiO_5 + 0.8\% Nd^{3+}$, $Y_2SiO_5 + 0.2\% Er^{3+}$, $Y_2SiO_5 + 0.1\% Yb^{3+}$ was carried out at frequencies of about 24 and 9 GHz. The SLR times (T_1) which were longer than 10^{-5} s were measured by the pulse saturation technique, and the times that were shorter than 10^{-7} s were derived from the spin–lattice broadening of the EPR lines according to the formula $T_1^{-1} = 1.4 \times 10^6 \pi g \Delta H_{s,ph}$ [11], where g is the g -factor and $\Delta H_{s,ph}$ is the spin–phonon broadening of the EPR lines in gauss. The results of the measurement are presented in fig. 2. Taking into consideration the contributions of the direct, Raman and Orbach process, the spin–lattice relaxation rate in all the cases are well fitted by the expression

$$T_1^{-1} = AT + CT^9 f\left(\frac{\theta_{slr}}{T}\right) + B e^{-\Delta/T}, \quad (1)$$

where θ_{slr} is the Debye local temperature [12], and Δ is the position of the first excited Stark level. The parameters A , B , C , and Δ are given in table II. The function $f(\theta_{slr}/T)$ in eq. (1) was used when experi-

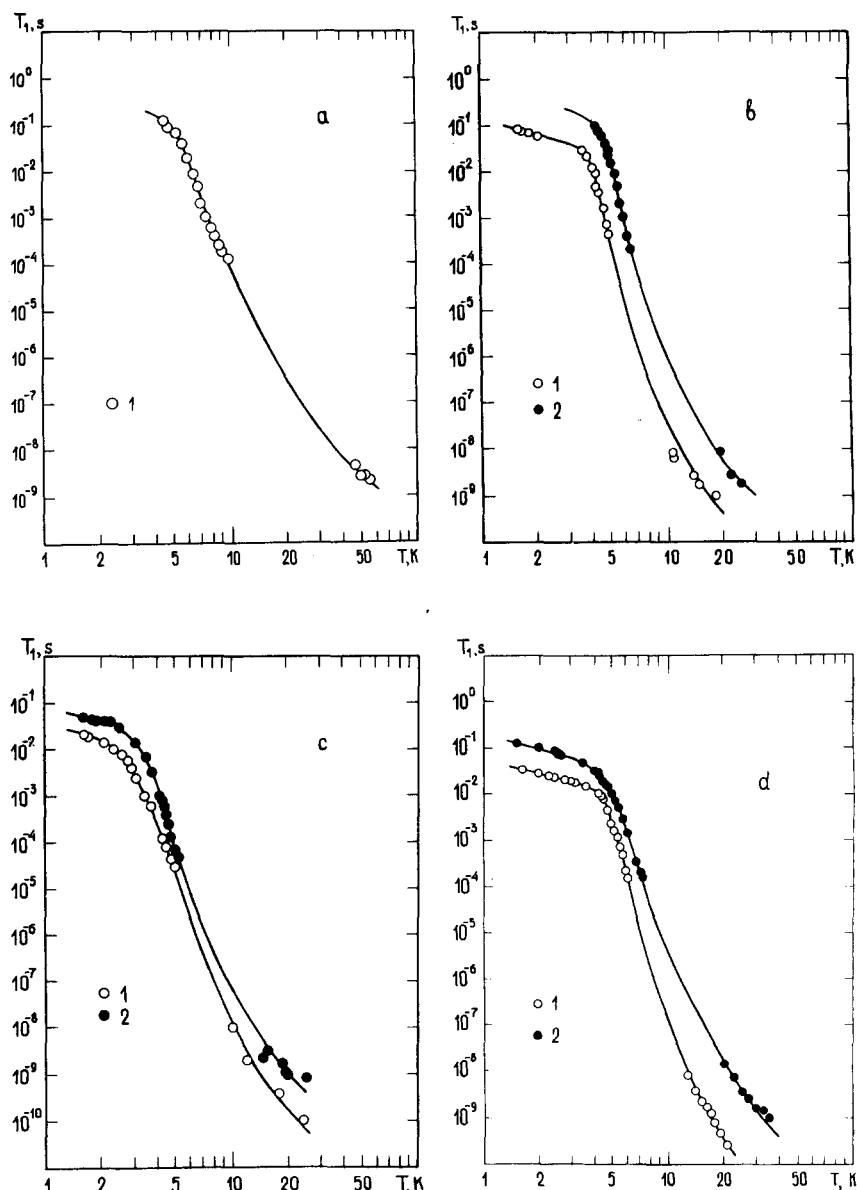


Fig. 2. The spin-lattice relaxation times of RE^{3+} ions in Y_2SiO_5 . (a) Ce^{3+} , orientation $H_0 \parallel z$, $\nu \approx 9$ GHz; (b) Nd^{3+} , orientation $H_0 \parallel z$, $\nu \approx 24$ GHz; (c) Er^{3+} , arbitrary orientation, $\nu \approx 9$ GHz; (d) Yb^{3+} , orientation $H_0 \parallel z$, $\nu \approx 24$ GHz. (1) Centres of type I; (2) centres of type II. Solid lines correspond to a dependence (1) with parameters given in table II.

mental values of T_1 were longer than these following from a $T_1^{-1} = CT^9$ dependence; this is possible in the case of a deviation of the Raman process from the $T_1^{-1} = CT^9$ law because of a violation of the $T \ll \theta$ condition. The values of $f(\theta_{sr}/T)$ were taken from ref. 13. It should be noted that $f(\theta_{sr}/T)$ can be intro-

duced very ambiguously as in the described temperature range where the Raman and Orbach processes take place simultaneously. We took the function $f(\theta_{sr}/T)$ with the highest possible value of θ_{sr} .

Unfortunately, the Debye temperature for Y_2SiO_5 is unknown, but for such a hard crystal [2,6,8] it

Table 2
The SLR data of rare-earth ions in Y_2SiO_5 single crystals

Ion	Centre type	A	C	B	Δ (K)	θ_{SLR} (K)	Experimental conditions
Ce^{3+}	I	1.6	4×10^{-6}	1.5×10^8	97	230	$H_0 \parallel z, \nu \approx 9$ GHz
	II	—	—	—	—	—	—
Nd^{3+}	I	7.7	$\leq 5.7 \times 10^{-5}$	6.2×10^{11}	94	—	$H_0 \parallel z, \nu \approx 24$ GHz
	II	1.4	$\leq 1.2 \times 10^{-5}$	3.8×10^{10}	97	—	$H_0 \parallel z, \nu \approx 24$ GHz
Er^{3+}	I	27	1.4×10^{-2}	2.4×10^{11}	83	150	arbitr. orient. $\nu \approx 9$ GHz
	II	11.7	1.3×10^{-3}	2.5×10^{10}	74	190	arbitr. orient. $\nu \approx 9$ GHz
Yb^{3+}	I	17.4	3×10^{-5}	9×10^{11}	107	—	$H_0 \parallel z, \nu \approx 24$ GHz
	II	5.4	2.5×10^{-5}	10×10^9	97	250	$H_0 \parallel z, \nu \approx 24$ GHz

should probably be close to ≈ 700 K. The obtained θ_{slr} values are considerably less than this value, which has been repeatedly observed in spin–lattice relaxation [12].

The first thing that demands attention is the large difference between T_1 for different centres (fig. 2). In all cases the centres with higher SLR rate belong to the type of centres with a greater g_n value, which to a certain extent confirms the correctness of the above mentioned division of centres.

For the Ce^{3+} ion the temperature dependence of T_1 was measured for the Ce_I^{3+} centre only. The temperature dependence of T_1 for Ce_{II}^{3+} was not studied, because of the influence on the spin–lattice relaxation of the non-resonance cross-relaxation through the fast relaxing Er^{3+} ions, which were found in a sample as some uncontrolled foreign impurity. The temperature dependence of T_1 changed with the sample orientation in a steady magnetic field. At 70 K, when cross-relaxation did not influence the results, T_1 was obtained from the EPR line broadening and turned out to be equal to 4×10^{-9} s, i.e. approximately four times as long as for the Ce_I^{3+} centre at the same temperature. This allowed us to classify the given centre as a slow-relaxation one.

It follows from the contributions to a relaxation rate of the Orbach process that the magnitudes of Δ for both centres of each ion are almost equal (table II). Both Δ and g_z differ by approximately 10% for

different centres. A greater g_z value corresponds to the centres with a greater Δ value.

It is necessary to note that such slight Δ changes for different centres cannot account for strong differences in T_1 , since the B coefficients in this case for different centres would differ by approximately $\approx 30\%$, and the C coefficients by approximately $\approx 40\%$, because $B_I/B_{II} \approx (\Delta_I/\Delta_{II})^3$ and $C_I/C_{II} \approx (\Delta_{II}/\Delta_I)^4$ [11]. One cannot assume either that such a difference in T_1 occurs only due to sound velocity changes v_{SLR} , for in such a case $C_I/C_{II} = (B_I/B_{II})^2$ regularity would be observed as $C \approx v_{SLR}^{10}$ and $B \approx v_{SLR}^5$. This, however, is not found in experiments. Apparently, the large differences in T_1 for different centres could be explained by taking into consideration all the factors which determine the spin–lattice relaxation rate.

The investigation of the EPR spectra and spin–lattice relaxation times of RE^{3+} centres showed that a difference between the Y_1 and Y_2 positions becomes strongly apparent at SLR times of paramagnetic centres corresponding to these positions. This is why the T_1 temperature dependences of RE^{3+} centres was considered to be the main distinguishing feature of the Y_1 and Y_2 positions. In accordance with this, all the fast relaxing centres were attributed to one type of activated centres which we labelled as RE_I^{3+} , and all the slow relaxing centres were attributed to the other type of centres, labelled RE_{II}^{3+} .

5. Summary

(1) As a result of the EPR spectra study of Ce^{3+} , Nd^{3+} , Er^{3+} and Yb^{3+} ions in Y_2SiO_5 , RE^{3+} ions were found to be substituted in both the Y_1 and Y_2 positions.

(2) The proximity of g_{max} -values and also the positions of the nearest excited Stark levels for both RE^{3+} centres allows us to assume that static crystal fields at Y_1 and Y_2 positions differ little in a Y_2SiO_5 crystal.

(3) It follows from the temperature dependences of the SLR times that the spin–lattice interactions of RE_1^{3+} and RE_2^{3+} centres are essentially different.

Acknowledgement

The authors express their sincere thanks to R.Yu. Abdulsabirov for experimental assistance. We are indebted to the late A.M. Morosov who provided us with single crystals and showed much interest in the crystal EPR spectroscopy.

References

- [1] N.A. Toropov et al., in: N.A. Tropov, ed., *Silicates of Rare-Earth Elements and their Analogs* (Publ. Nauka, 1971) [in Russian].
- [2] E.K. Keller and A.K. Kuznetsov, *Zh. Prikl. Khim.* 35 (1962) 250.
- [3] L.A. Harries and C.B. Finch, *Amer. Miner.* 50 (1965) 1493.
- [4] C. Michel, G. Buisson and E.F. Bertaut, *Compt. Rend* and 264B (1967) 397.
- [5] B.A. Maximov, Yu.A. Charitonov, V.V. Ilyukhin and N.B. Belov, *Dokl. Akad. Nauk SSSR, Ser. Mat. Fiz.* 183 (1968) 1072.
- [6] I.A. Bondar, A.A. Lokpakov, L.Yu. Markovsky, A.N. Sokolov, L.E. Tarasova and N.A. Tropov, *Izv. Akad. Nauk SSSR, Ser. Fiz.* 33 (1969) 1057.
- [7] Kh.S. Bagdasarov, A.A. Kaminsky, A.M. Kevorkov, A.M. Prokhorov, S.E. Sarkisov and T.A. Tevosyan, *Dokl. Akad. Nauk SSSR* 212 (1973) 1326. (*Sov. Phys. Dokl.* 18 (1974) 664).
- [8] P.A. Arsenev, L.N. Raiskaya and R.K. Sviridovaya, *Phys. Status Solidi (a)* 13 (1972) 45.
- [9] N.M. Nizamutdinov, G.R. Bulka and V.M. Vinokurov, in: *Composition Structure and Properties of Minerals* (Publ. Kazan State Univ., 1973) [in Russian].
- [10] S.A. Al'tshuler and B.M. Kozyrev, *Electron Paramagnetic Resonance* (Publ. Nauka, Moskva, 1972) [in Russian].
- [11] A.A. Antipin, A.N. Katyshev and I.N. Kurkin, in: *Paramagnetic Resonance* (Publ. Kazan State Univ., 1971) [in Russian].
- [12] I.N. Kurkin, E.A. Tsvetkov, K.P. Chernov and Yu.K. Chirkin, *Fiz. Tverd. Tela* 18 (1976) 2931.
- [13] I.N. Kurkin, Yu.K. Chirkin and V.I. Shlenkin, *Fiz. Tverd. Tela* 14 (1972) 2719 (*Sov. Phys.* 14 (1973) 2348).