

Hyperfine interaction of V_k centres in Cs_2NaYCl_6 crystals

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In this work we present the results obtained through electron paramagnetic resonance (EPR) spectroscopy of the study of the hyperfine interaction of the V_k centres in the Cesium, sodium, yttrium hexachloride (Cs_2NaYCl_6) crystals. These electron defect centres are created by γ -irradiation at liquid nitrogen temperature of the Cs_2NaYCl_6 crystals. Our results are: $g_{\parallel}=2.008$, $g_{\perp}=2.023$, $A_{\parallel}=91.21$ (gauss) and $A_{\perp}=3.10$ (gauss) and these results are compared with those obtained by Th. Pawlik and J.M. Spaeth [24] for the same system and those of D. Shoemaker [23] for sodium chloride.

Keywords: Elpasolites; crystal growth; colour centres; EPR.

Presentamos los resultados obtenidos por medio de la espectroscopia de resonancia paramagnetica electronica (EPR) del estudio de la interaccion hiperfina de centros V_k en los cristales de hexacloruro de cesio, sodio, itrio (Cs_2NaYCl_6). Estos centros de defecto electronico se crean por irradiacion γ a temperatura de nitrogeno liquido en los cristales de Cs_2NaYCl_6 . Nuestros resultados son: $g_{\parallel}=2.008$, $g_{\perp}=2.023$, $A_{\parallel}=91.21$ (gauss) and $A_{\perp}=3.10$ (gauss) y estos resultados se comparan con los obtenidos por Th. Pawlik y J.M. Spaeth [24] para el mismo sistema y los de D. Shoemaker [23] para cloruro de sodio.

Descriptor: Elpasolitas; crecimiento de cristales; centros de color; EPR.

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1. Introduction

Elpasolites with chemical formula Cs_2NaRX_6 (being trivalent R a member of the rare earth, actinide or transition-metal ions; and X an halogen ion) have been subject to numerous optical [1-6], magnetic studies [7-12], and other techniques [13-16]. They normally exhibit cubic symmetry at room temperature. The unit cell could be described as constituted by six negatively charged halogen ions located at the corners of an octahedron in whose centre is located the trivalent ion (R). Each one of the X^- ions that form the octahedral are located at the centre of each face of a cube in whose corners are located C_s^+ ions. Those C_s^+ ions occupy the centre of a cube in whose corners are located Na^+ and R^{3+} ions in alternate positions. Elpasolites have been widely studied because of the fact that they are iso-structural; thermally and chemically stable and they can usually be grown as single crystals and, the most interesting fact is the perfect O_h^5 site symmetry for trivalent ions (R) without the necessity of charge compensation. On the other hand, the subject of this work, the V_k center (self-trapped hole), have been subject to very few investigations in the elpasolites. The V_k centre in the alkali halides was first investigated by Känzig [17] by electron paramagnetic resonance (EPR) in x-irradiated KCl crystals at liquid nitrogen temperatures. The study by EPR of the V_k center in several alkali halides were investigated by several workers [18-23]. All these investigations using EPR and electron nuclear double resonance (ENDOR) spectroscopies showed that the V_k center is a negatively charged halide molecule with the molecular axis lying along a [110] crystallographic direction. There is a recent work [24] on the hexachloride elpasolite of cesium, sodium and yttrium,

in which V_k centers are detected by EPR spectroscopy when these crystals are subject to x-irradiation at liquid nitrogen temperatures. The purpose of this paper is to measure the hyperfine interaction, by EPR spectroscopy, of the electron defects created by γ -irradiated $Cs_2NaYCl_6:Gd^{3+}$ crystals at liquid nitrogen temperatures and make a comparison of these results with those by x-irradiation in the same system and in the alkali halides. We have chosen for this work the yttrium elpasolite because in the 6 to 473 K temperature interval no phase changes has been detected [25] and this simplifies the study of the V_k centre.

2. Experimental procedure

Using the procedure described by L.R. Morss [26] we have prepared the compound Cs_2NaYCl_6 from yttrium oxide (Rhone-Poulenc), sodium chloride (J.T. Baker) and cesium chloride (Alfa Aesar), all of them reagent grade raw materials, by mixing the appropriate stoichiometric amounts. The YCl_3 was prepared from Y_2O_3 by standard chemical methods. Once the compound is sublimated, it is introduced in a quartz capsule which is evacuated at a pressure of 1.33×10^{-3} Pa. The crystal is then grown using the Bridgman method at a temperature of 1200 K and a growth velocity of 3 mm/hr. The resulting crystal does not present cleavage planes. The crystal is oriented on the plane (110), which is achieved by means of an angular variation of the electron paramagnetic resonance spectrum of the ion Gd^{3+} , impurity present in the system (in very low concentration) due to the yttrium oxide and not added as an intentional impurity. Since the EPR spectrum of the Gd^{3+} ion is well known, the angular variation of this spectrum allows us to establish the crystal-

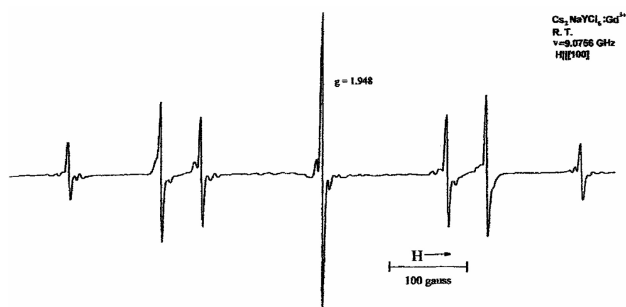


FIGURE 1. EPR spectrum of the system $\text{Cs}_2\text{NaYCl}_6:\text{Gd}^{3+}$ at room temperature. The external magnetic field \mathbf{H} is parallel to the $[100]$ crystallographic direction.

line plane and the direction in which the static magnetic field is lying. Figure 1, shows the EPR spectrum of the $\text{Cs}_2\text{NaYCl}_6:\text{Gd}^{3+}$ crystal at room temperature, without γ -irradiation, with the static magnetic field parallel to the $[100]$ direction. Once the proper crystallographic plane in the sample has been identified, the sample was irradiated in a cryostat containing liquid nitrogen in a γ beam system (model 651 PT) during 20 hours at a rate of 10.28 kGy/hr. Once the crystal has been γ -irradiated it is placed in the sample holder [27] which allows us to keep the sample at 77 K or below. The EPR studies of the V_k centre have been carried out in a JEOL (JES-RE3X) spectrometer. The temperature of the sample was monitored with an ITC502 (Oxford) temperature controller. The sample temperature was kept at 44 K in order to guarantee the permanency of the V_k centres.

3. Results and discussion

Using EPR spectroscopy we have detected V_k colour centres in the elpasolite $\text{Cs}_2\text{NaYCl}_6$ crystals γ -irradiated at liquid nitrogen temperature and observed also at this and lower temperatures. Känzig [17] showed that the V_k centre in the alkali halides is an electronic defect produced by the displacement of a p electron from the chlorine ions forming in this way a Cl_2^- molecule. In the elpasolite under study the V_k centre follows the same formation mechanism. Since the V_k centre is a self-trapped hole in a pair of negative ions, we have that the effective electronic spin is equal to $(1/2)\hbar$ so, if this is the situation we have only one magnetic dipolar transition. Nevertheless, if the nuclei of the negative ions have non-zero nuclear spin we should observe by EPR spectroscopy the hyperfine interaction (hf) among the hole and the halogen nuclei. In our case, for the $\text{Cs}_2\text{NaYCl}_6$ elpasolite, the negative ions in which the hole is trapped are the chlorine ions. Since there are two isotopes of chlorine, ^{35}Cl and ^{37}Cl , with 75% and 25 % abundance respectively, both with nuclear spin $(3/2)\hbar$. We will have the following possible arrangements of molecule/ions: $^{35}\text{Cl}-^{35}\text{Cl}$, $^{35}\text{Cl}-^{37}\text{Cl}$, $^{37}\text{Cl}-^{35}\text{Cl}$ and $^{37}\text{Cl}-^{37}\text{Cl}$. We observed that the symmetry axis of the centres lies along the $\langle 110 \rangle$ crystal axes, that is, along the Cl-Cl axis. The EPR spectrum of the V_k centre can be described by the following spin Hamiltonian:

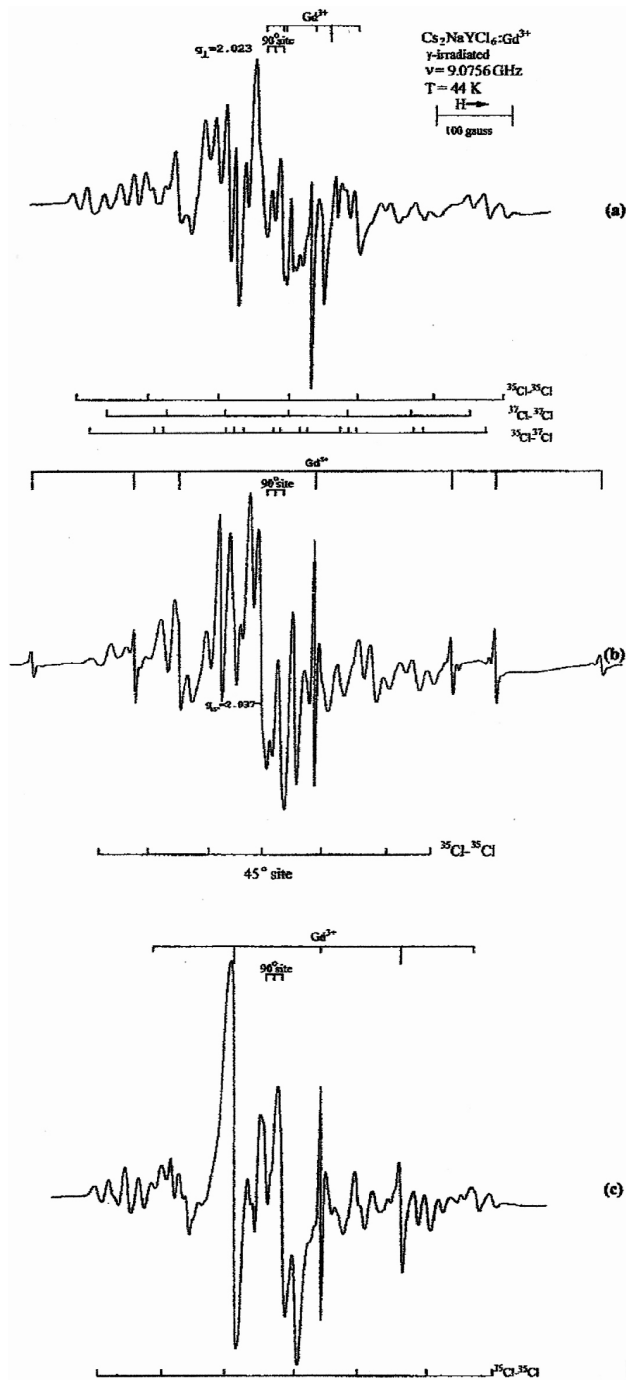


FIGURE 2. EPR spectrum of the system $\text{Cs}_2\text{NaYCl}_6:\text{Gd}^{3+}$ γ -irradiated at liquid nitrogen temperature. The spectra were taken at 44 K: (a) The external magnetic field is parallel to the $[110]$ crystallographic direction; (b) the external magnetic field lies parallel to the $[100]$ crystallographic direction; (c) the external magnetic field is parallel to the $[111]$ crystallographic direction.

$$\mathcal{H} = \mu_\beta \bar{H} \cdot \bar{g} \cdot \bar{S} + \sum_{i=1}^2 \bar{I}_i \cdot \bar{A} \cdot \bar{S}$$

where \bar{H} is the external magnetic field, μ_β is the Bohr's magneton, \bar{g} the spectroscopic factor, \bar{S} the electron spin vector

TABLE I. Results of this research and comparison with other authors

V_k centre in:	g_{\parallel}	g_{\perp}	A_{\parallel} (gauss)	A_{\perp} (gauss)	Ref.
Cs_2NaYCl_6	2.008(1)	2.023(1)	91.21(4)	3.10(5)	This work
Cs_2NaYCl_6	2.001(1)	2.036(1)	96.42(5)	4.29	[24]
NaCl	2.0010(1)	2.0458(1)	98.71(5)	9.04	[23]

operator, \bar{I} is the nuclear spin vector operator, \bar{A} is the hyperfine tensor and the sum runs over the two Cl nuclei. In order to obtain values of the spin Hamiltonian parameters the energy matrix were solved in an exact form. For each measured resonance field position, a least square fit of all spin-Hamiltonian parameters was made by a computer program which adjusted these parameters until the computed transition energies were equal or less than the experimental error in the measured microwave energy used in the experiment. The obtained parameters are shown in Table I. Figure 2a shows the EPR spectrum of the V_k centre at 44 K with the external magnetic field applied parallel to the [110] crystallographic direction. In this spectrum we have identified the different sites of the V_k centre. The site identification has been achieved by means of an angular variation in the plane (110) (Fig. 3), which has allow us to determine the angular distribution of a portion of the V_k center that belong to the ^{35}Cl - ^{35}Cl , molecule-ion. ^{37}Cl - ^{37}Cl has the same angular behavior but with smaller splitting. ^{35}Cl - ^{37}Cl , for non equivalent nuclei we report the 16 transitions (Fig. 1a) but is very difficult with our means to follow them during the angular variation in the (110) plane. When H is lying parallel to [110] the crystallographic direction it is possible to identify three contributions to the EPR spectrum: a contribution of the parallel site with abundance one, the contribution of the site parallel to the $[1\bar{1}0]$ crystallographic direction which is perpendicular to the external magnetic field (90° site), also with abundance one and, the contributions of sites parallel to crystallographic $\langle 110 \rangle$ directions which make a 60° angle with respect to the external magnetic field H , and having abundance 4, (see Fig. 2a). In this figure we have identified the spectrum that corresponds to the centers ^{37}Cl - ^{37}Cl , ^{35}Cl - ^{37}Cl and ^{35}Cl - ^{35}Cl . This was possible because in this magnetic field orientation we have the maximum splitting of the spectrum and there is less overlap between transitions that comes from each contribution. This does not occur when the external magnetic field lies parallel to the [100] or to the [111] directions since for these orientations it is not possible to observe the spectrum lines arising from the centers ^{37}Cl - ^{37}Cl ; ^{35}Cl - ^{37}Cl . When the external magnetic field is parallel to the [100] crystallographic direction the EPR spectrum presents two contributions: a perpendicular one which comes from the $[1\bar{1}0]$ and $[110]$ crystallographic directions with abundance two, and a second contribution that come from the sites at 45° with respect to the external magnetic field, this contribution is of abundance 4, (Fig. 2b). When the external magnetic field lies parallel to the [111] crystallographic direction we

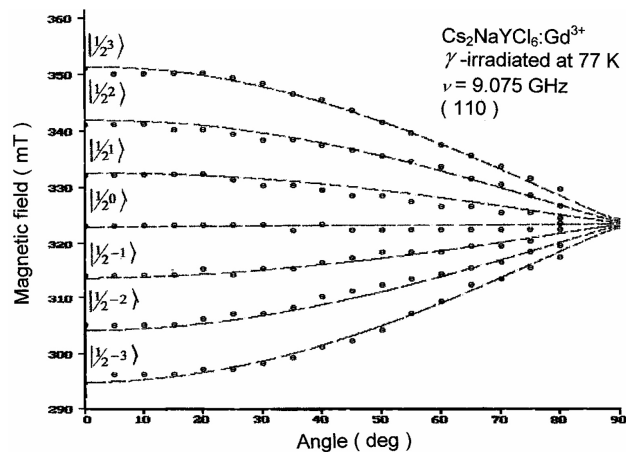


FIGURE 3. Angular variation for the magnetic field lying in the (110) crystallographic plane. The transitions correspond to the V_k sites. The kets represent the final state of the transition. The angular variation was done at 44 K. The circles correspond to the experimental measurements and the dashed lines to the theoretical calculation.

have two contributions to the EPR spectrum: the perpendicular one which comes from $[1\bar{1}0]$, $[10\bar{1}]$ and $[01\bar{1}]$ crystallographic directions, with an abundance of 3, and the contribution of the sites parallel to the $\langle 110 \rangle$ crystallographic directions and forming a $35^\circ 44'$ angle with the $[111]$ crystallographic direction and with an abundance 3. (Fig. 2c). From the angular variation in the (110) crystallographic plane it is observed that the contribution of the $[1\bar{1}0]$ crystallographic direction presents no angular variation and that the contribution is one when H is parallel to the $[110]$ crystallographic direction, three when H is parallel to the $[111]$ crystallographic direction and finally two when H is parallel to the $[110]$ crystallographic direction. With this information it was possible to identify the perpendicular site (90° site). In Table I we report the values of the spectroscopic factor g and the hyperfine constant A obtained in this work in comparison to those obtained by Pawlik and Spaeth [24].

4. Conclusions

In this work we present measurements of the spin Hamiltonian hyperfine parameters for the V_k center formed by γ -irradiation at liquid nitrogen temperature in the $Cs_2NaYCl_6:Gd^{3+}$ elpasolite. These results differ from those published for this same system [24] and comparison with the results of this work is difficult because the authors only present the EPR spectra in the [100] crystallographic direc-

tion and the angular variation with the crystal rotated in the $(00\bar{1})$ plane is not very clear. In Pawlik and Spaeth paper [24] they report a g_{\perp} value of the 45° site which does not correspond to the perpendicular site of the V_k center, so, we think this difference in the results is probably because a misinterpretation of the spectra involved in the different crystallographic directions. Since, in general, the V_k centre has been modeled as a hole trapped in the electronic levels of a halo-

gen molecule/ion (Cl_2^-) it is important to study the influence of the crystalline neighborhood and not to be considered as an isolated defect. So, there is much information to be obtained from this problem. On the other hand, the sample holder used in this investigation allows us to have many possibilities for the study of radiation induced defects at low temperatures in materials to be analyzed by EPR spectroscopy and, possibly, another spectroscopies.

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