Elpasolites with chemical formula Cs$_2$NaRX$_6$ (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 octahedron 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$_{6}^k$ 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 $\gamma$-irradiated Cs$_2$NaYCl$_6$: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$_2$NaYCl$_6$ 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$_2$O$_3$ 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 $\times$ 10$^{-3}$ Pa. The crystal is then grown using the Bridgeman 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-
line plane and the direction in which the static magnetic field is lying. Figure 1, shows the EPR spectrum of the Cs$_2$NaYCl$_6$: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 Cs$_2$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 Cs$_2$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: $^{35}$Cl-$^{35}$Cl, $^{35}$Cl-$^{37}$Cl, $^{37}$Cl-$^{35}$Cl and $^{37}$Cl-$^{37}$Cl. We observed that the symmetry axis of the centres lies along the (110) 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:

$$
\mathcal{H} = \mu_\beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \sum_{i=1}^{3} T_i \cdot \mathbf{A} \cdot \mathbf{S}
$$

where $\mathbf{H}$ is the external magnetic field, $\mu_\beta$ is the Bohr’s magneton, $\mathbf{g}$ the spectroscopic factor, $\mathbf{S}$ the electron spin vector.
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 \(V_k\) centers that belong to the \(^{35}\text{Cl}-^{35}\text{Cl}\), molecule-ion. \(^{37}\text{Cl}-^{37}\text{Cl}\) has the same angular behavior but with smaller splitting. \(^{35}\text{Cl}-^{37}\text{Cl}\), 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 [110] crystallographic direction which is perpendicular to the external magnetic field (90° site), also with abundance one and, the contributions of sites parallel to crystallographic (110) 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 \(^{37}\text{Cl}-^{37}\text{Cl}\), \(^{35}\text{Cl}-^{37}\text{Cl}\) and \(^{35}\text{Cl}-^{35}\text{Cl}\). 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 \(^{37}\text{Cl}-^{37}\text{Cl}\); \(^{35}\text{Cl}-^{37}\text{Cl}\). 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 [110] 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 have two contributions to the EPR spectrum: the perpendicular one which comes from [110], [011] and [011] crystallographic directions, with an abundance of 3, and the contribution of the sites parallel to the (110) crystallographic directions and forming a 35° 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 [110] 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].

### Table I. Results of this research and comparison with other authors

<table>
<thead>
<tr>
<th>(V_k) centre in:</th>
<th>(g_\parallel)</th>
<th>(g_\perp)</th>
<th>(A_\parallel) (gauss)</th>
<th>(A_\perp) (gauss)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs(_2)NaYCl(_6)</td>
<td>2.008(1)</td>
<td>2.023(1)</td>
<td>91.21(4)</td>
<td>3.10(5)</td>
<td>This work</td>
</tr>
<tr>
<td>Cs(_2)NaYCl(_6)</td>
<td>2.001(1)</td>
<td>2.036(1)</td>
<td>96.42(5)</td>
<td>4.29</td>
<td>[24]</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.0010(1)</td>
<td>2.0458(1)</td>
<td>98.71(5)</td>
<td>9.04</td>
<td>[23]</td>
</tr>
</tbody>
</table>

#### 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 corresponds to the experimental measurements and the dashed lines to the theoretical calculation.

### 4. Conclusions

In this work we present measurements of the spin Hamiltonian hyperfine parameters for the \(V_k\) center formed by \(\gamma\)-irradiation at liquid nitrogen temperature in the Cs\(_2\)NaYCl\(_6\)-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 (001) 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 halogen molecule/ion ($\text{Cl}_2^-$) 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.