Sample holder for measurement at very low temperatures by electron paramagnetic resonance spectroscopy

J. Barreto, J.L. Boldú, H. del Castillo, R. Gleason, and E. Muñoz P.
Instituto de Física, Universidad Nacional Autónoma de México,
Apartado Postal 20-364, México, D.F. 01000, Mexico,
e-mail: jorgeb@fisica.unam.mx

Recibido el 24 de noviembre de 2008; aceptado el 17 de abril de 2009

In this paper we describe the design and use of a sample holder for measurements of colour centers in elpasolite crystals irradiated at liquid nitrogen temperatures and measured at the same temperature by electron paramagnetic resonance spectroscopy.

Keywords: Defects in solids; γ-irradiation; electrón paramagnetic resonance.

Se presenta el diseño y uso de un portamuestras para mediciones de centros de color en cristales de elpasolita irradiados a temperaturas de nitrógeno líquido y medidos a la misma temperatura por medio de espectroscopía de Resonancia Paramagnética Electrónica.

Descriptores: Defectos en sólidos; irradiación γ; resonancia paramagnética electrónica.

PACS: 61.80.-x; 76.30.-v; 61.72.jn; 07.20.Mc

1. Introduction

In the study of monocrystalline samples by electron paramagnetic resonance (EPR) there are two fundamental parameters: the temperature and the crystal orientation with respect to the external magnetic field [1-4]. In experiments where it is necessary the variation of the crystal temperature and its orientation with respect to the external magnetic field the crystal sample is placed in a sample holder made of a quartz rod in such a way that the surface of the quartz rod where the crystal is placed is a plane in order to keep the sample in a vertical plane against a possible twist. The simplest way to fix the crystal is with an adhesive that does not present any EPR signal. For temperatures higher than 100°C the adhesive decomposes and the crystal placed in the sample holder falls into the resonant cavity. It is necessary to point out that in the above procedure the initial sample temperature is room temperature at which it is simple to place the sample on the sample holder. A very different situation is when it is necessary to maintain the sample, when it has to be placed on the sample holder, at a temperature lower than room temperature. An experiment that presents this situation is when the samples have to be irradiated at temperatures lower than room temperature and also it is necessary to keep them at such low temperature since an increase in temperature signifies the loss of information produced by the irradiation of the sample. This paper describes the design and use of a sample holder that makes it possible to handle and maintain the sample under study at liquid nitrogen temperature without using any kind of adhesive.

2. Experiment

In order to produce V_k centres in the Cs_2NaYCl_6:Gd^{3+} [5,6] elpasolite single crystal samples, in which we have identified a (110) plane by means of an angular variation of the Gd^{3+} EPR transitions , the crystal is irradiated in a $\gamma-$beam, model 651 PT at a dose rate of 10.28 kGy/hr, for 20 hours. During the entire irradiation process the samples remain at liquid nitrogen temperature. To carry out the EPR study of the V_k centres it is necessary to keep the sample at the irradiation temperature when it is introduced into the resonance cavity

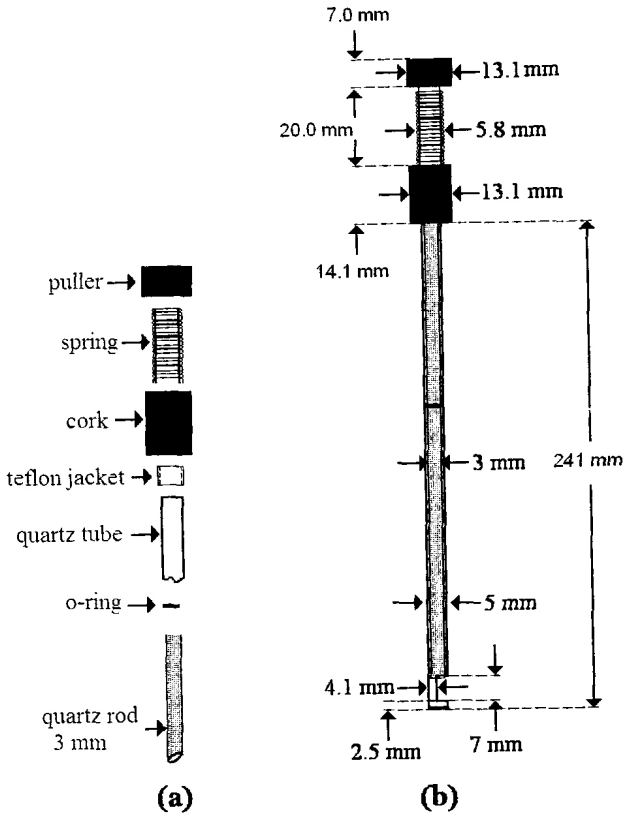

FIGURE 1. Schematic diagram of sample holder in which it is possible to keep the crystalline sample at a low temperature in the EPR resonant cavity.

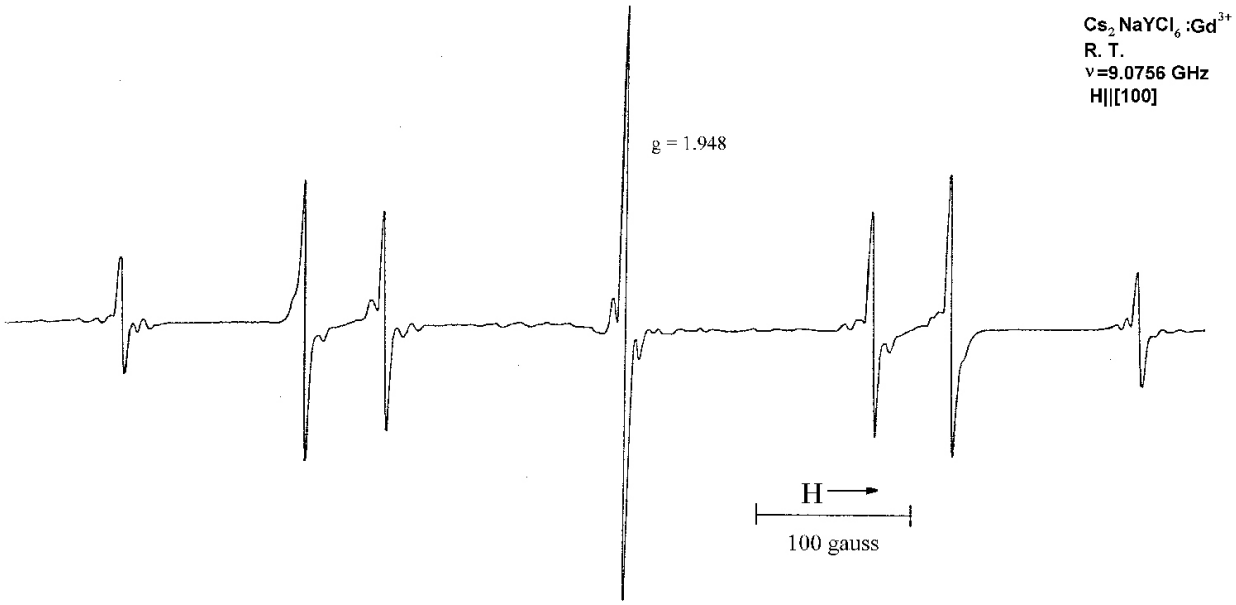

FIGURE 2. EPR spectrum of Gd^{3+} in Cs_2NaYCl_6 crystal at room temperature. The external magnetic field is parallel to the [100] crystallographic direction.

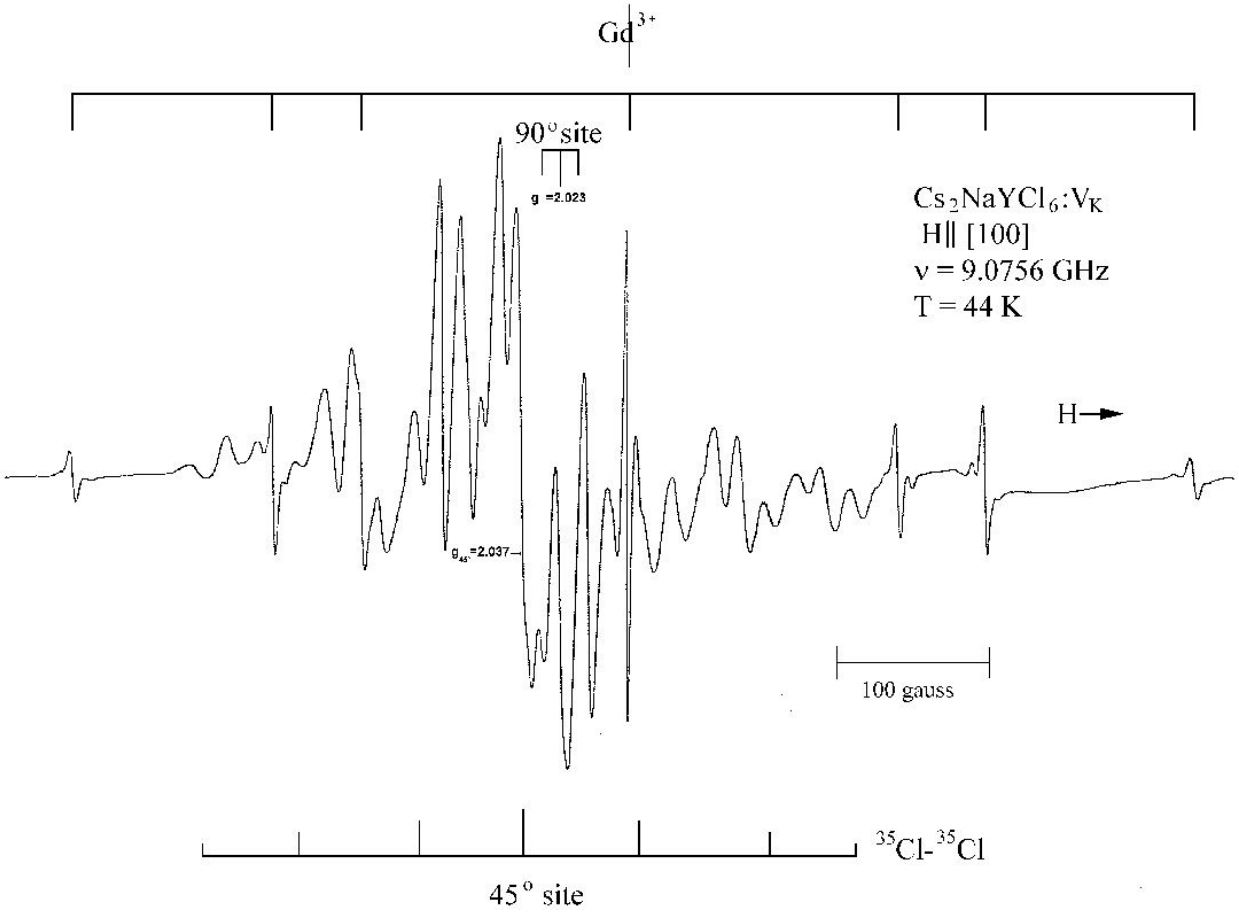

FIGURE 3. EPR spectrum of the same sample of Fig. 2 after being $\gamma-$irradiated at liquid nitrogen temperature. The spectrum is taken at 44 K with the external magnetic field along the [100] direction of the crystal.

since, as was pointed out earlier, taking the sample out the liquid nitrogen container in which it was irradiated and gluing it on the sample holder means the loss of the information produced by the irradiation in the crystal. The solution to this problem is the design and construction of a quartz sample holder that makes it possible to maintain the sample at liquid nitrogen temperature with the possibility of maintaining the original crystal orientation when it is placed in the spectrometer cavity. In Fig. 1 we present the schematic diagram of the sample holder.

3. Sample holder description

One end of the quartz tube with a 5 mm outer diameter, 4 mm inner diameter and length of 250 mm (sample holder jacket) is sealed in such a way that the bottom is even. At a distance of 2.5 mm. from the bottom, which is a plane, a recess is made by means of a silicon carbide rectangular bar as shown in Fig. 1b. This tube is placed in an aluminum barrel which is fixed to a teflon jacket to avoid stresses produced when using an adhesive. This is shown in Fig. 1a. In order to displace, the quartz rod of 3 mm diameter along the quartz jacket, thus maintaining the sample in place by mechanical pressure, the quartz rod is cemented (glued) to the aluminum barrel with a cianoacrylate based adhesive. The puller is fixed to the two aluminum pieces introducing its ends into 1 mm diameter holes. Since low pressure is required in the system, in order to establish a helium flux, it is necessary to guarantee a sealed system and this is accomplished by placing an o-ring between the rod and the jacket covered with Apieson N grease for a vacuum. Once the crystal sample has been irradiated at a low temperature it is placed in a vessel containing liquid nitrogen large enough so that it can contain the lower end of the sample holder. The sample holder is introduced into the vessel in which the quartz rod has been displaced by means of the puller in such a way that the irradiated crystal, with the aid of dissection pliers, is placed in the recess of the quartz tube (Fig. 1b). At this point it is necessary to be careful to place the sample in the required orientation that was previously selected and marked. Once the crystal has been placed, the rod is allowed to press it, being careful not to modify the crystal orientation. The space between the jacket and the pressing rod has previously been filled with liquid nitrogen which makes it possible to keep the sample at a low temperature while being placed in the resonance cavity which was previously equipped with the low temperature system (*i.e.* Oxford ESR 900). Since the crystal sample is kept in place in the quartz sample holder without using any type of adhesive, it can be used from very low temperature (4 K) up to temperatures as high as 1000 K.

4. Use of the sample holder

A study of the V_k center has been done on Cs_2NaYCl_6 crystals [6]. The cesium, sodium, and yttrium hexachloride compounds were obtained following the process described by L.R. Morss [7,8] and the crystals were grown by the Bridgman method. Before irradiation, an angular variation is done to determine the plane in which the study will be done. In order to produce V_k centers in these crystals it is necessary to keep the sample at liquid nitrogen temperature during the γ-irradiation. Once the γ-irradiation is concluded, it is important to keep the sample at liquid nitrogen temperature. Figure 2 shows the EPR spectrum of Gd^{3+} in Cs_2NaYCl_6 taken at room temperature with the external magnetic field along the [100] crystallographic direction before the sample irradiation. The spectrum shows the seven EPR transitions due to the ion Gd^{3+} (S= 7/2) in cubic crystalline symmetry which substitutes the yttrium trivalent ion. In Fig. 3 presents the EPR spectrum taken at 44 K with the sample placed in the sample holder after it has been irradiated at liquid nitrogen temperature. In this complex spectrum we have identified the different contributions made by the V_k centers produced by the irradiation. Since the V_k center is a self-trapped hole in a pair of negative ions, its efective spin is $1/2\hbar$ so we have only one dipolar transition, but since the nuclei of the negative ions , ^{35}Cl and ^{37}Cl , have non-zero nuclear spin (^{35}I = 3/2 and ^{37}I =3/2), we should observe by EPR spectroscopy the hyperfine interaction between the hole and the halogen nuclei. The detailed interpretation of this new spectrum is the topic of another paper that is going to be published soon.

Acknowledgments

We would like to thank Mr. Carlos Sanchez for his collaboration in the construction of the sample holder prototype. Dr. Epifanio Cruz and Fís. Francisco García for the irradiation of the samples, and DGAPA (México) for financial support under contract IN103500.

1. E. Wertz John and R. Bolton James, *Electron Spin Resonance, Elementary Theory and Practical Applications* (Mc Graw-Hill, 1972)
2. J.W. Orton. *Electron Paramagnetic Resonance* (Iliffe Books LTD. 1968).
3. R.S. Alger, *Electron Paramagnetic Resonance, Techniques and Applications* (Interscience Publishers, 1968).
4. A. Abragam, B. Bleaney. *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press. Oxford, 1970).
5. Th. Pawlik and J-M. Spaeth, *J. Phys. Condens. Matter* **9** (1997) 8737.
6. J. Barreto Renteria "Estudio por medio de Resonancia

Paramagnética Electrónica de defectos puntuales producidos por radiación ionizante" Tesis de maestría, Posgrado en Ciencia e Ingeniería de Materiales, Instituto de Investigaciones en Materiales, UNAM., MÉXICO, 2006.

7. L.R. Morss and Fuger J. *Inorganic Chemistry* **8** (1969) 1433.

8. L.R. Morss, M. Siegal, L. Stenger and Edelstein, *Inorganic Chemistry* **9** (1970) 1771.