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

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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.

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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 Cs2NaYCl6:Gd3+ [5,6] elpasolite single crystal samples, in which we have identified a (110 ) plane by means of an angular variation of the Gd3+

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\text{EPR transitions}, \text{ the crystal is irradiated in a } \gamma-\text{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.}
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Figure 2. EPR spectrum of Gd$^{3+}$ in Cs$_2$NaYCl$_6$ 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 glu-
ing 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 spectrom-
eter 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)
was 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 guaran-
tee 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 irra-
diated 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 crys-
tal, with the aid of dissection pliers, is placed in the recess
of the quartz tube (Fig. 1b). At this point it is necessary
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 cav-
ity 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$_2$NaYCl$_6$
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 Bridg-
man 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
$\gamma$-irradiation. Once the $\gamma$-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$_2$NaYCl$_6$
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 nitro-
gen temperature. In this complex spectrum we have identi-
fied the different contributions made by the $V_k$ centers pro-
duced by the irradiation. Since the $V_k$ center is a self-trapped
hole in a pair of negative ions, its effective spin is 1/2$\hbar$ so we
have only one dipolar transition, but since the nuclei of the
negative ions, $^{35}\text{Cl}$ and $^{37}\text{Cl}$, have non-zero nuclear spin
($^{35}\text{I} = 3/2$ and $^{37}\text{I} = 3/2$), we should observe by EPR spec-
troscopy the hyperfine interaction between the hole and the
halogen nuclei. The detailed interpretation of this new spec-
trum is the topic of another paper that is going to be published
soon.

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