EPR of borax-alanine mixtures irradiated with thermal neutrons

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Electron Paramagnetic Resonance (EPR) of neutron irradiated crystallite mixtures of alanine and borax is reported. These experiments are aimed at establishing an EPR dosimetry technique for thermal neutrons based on the resonance signal enhancement of alanine due to the boron content in the mixtures via a neutron capture reaction. Signal response as a function of boron content and crystallite size of the mixtures is presented.

Keywords: Electron paramagnetic resonance; free radicals; neutron dosimetry.

Se reporta la Resonancia Paramagnética Electrónica (EPR) de mezclas de alanina y borax irradiadas con neutrones. El objetivo de estos experimentos es establecer una técnica de dosimetría EPR para neutrones térmicos basada en el incremento de la señal de alanina debido al contenido de boro en las mezclas vía una reacción de captura neutrónica. Se presenta la respuesta de la señal como función del contenido de boro y del tamaño de los cristalitos de las mezclas.

Descriptores: Resonancia paramagnética; radicales libres; dosimetría de neutrones.
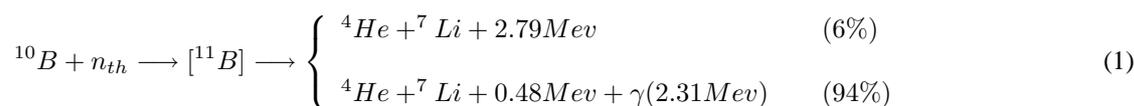
PACS: 76.30.Rn; 87.53.Pb

1. Introduction

The alanine EPR dosimetry system for γ-ray, and electron irradiation, provide a reliable procedure for measuring the absorbed dose. This well established procedure is based on the generation of the stable free radical $CH_3 - \dot{C}H - COOH$ in crystalline alanine by irradiation. Upon irradiation, the radical concentration increases in the dosimeters and the identification and concentration measurements are performed by Electron Paramagnetic Resonance (EPR) spectroscopy [1].

In spite of the success of the technique, the method has not been applied to thermal neutron dosimetric measurements. This is due to the fact that the energy deposition, of thermal neutrons in irradiated alanine produces a low number of radicals, and consequently the EPR signal of the alanine samples is exceedingly weak, hampering the use of the method as a thermal neutron dosimetry technique. To overcome this apparent difficulty, a billard-ball approach to enhance the EPR response of alanine to thermal neutron irradiation has been proposed [2].

This approach consists of mixing crystallites of a boron compound with alanine crystallites. In this way, when the mixture is irradiated, the ^{10}B isotopes of the compound may experience a neutron capture reaction yielding stripped down ^4He helium nuclei ($\alpha-$particles), $\gamma-$rays, and ^7Li nuclei,

$$^{10}B + n_{th} \longrightarrow [^{11}B] \longrightarrow \begin{cases} ^4He +^7 Li + 2.79 Mev & (6\%) \\ ^4He +^7 Li + 0.48 Mev + \gamma(2.31 Mev) & (94\%) \end{cases} \tag{1}$$

In this billard-ball approach, the cue-ball is the thermal neutron, and the α, γ , and ^7Li are the products of the "opening break". These products can, in turn, strip off other molecules, thus multiplying the number of projectiles. Subsequently these products can, in turn, strike an alanine crystallite, thus producing extra free radicals. Consequently the alanine EPR signal increases, hence the possibility of having an EPR thermal neutron dosimeter.

The usefulness of having an EPR thermal neutron dosimeter resides in the "mixed radiation field" area. A dosimeter, such as the one we are proposing, will respond simultaneously to thermal neutrons, electrons and gamma rays. In other words, in a "mixed field", its EPR signal intensity will be the sum of the effects of the mentioned irradiation.

Now, whenever we wish to evaluate these different irradiation contributions in a mixed radiation field, we put forward the following procedure. Together with the intended neutron dosimeter we can place two alanine dosimeters. Both with the same alanine content as the former dosimeter, but both without the boron compound, so they will be practically insensitive to thermal neutrons. In addition, one of the dosimeters of the latter pair should be shielded to electron irradiation, so its response will be exclusively due to gammas (in most cases a minor shield will prove sufficient).

When the proposed triplet of dosimeters is placed in the mixed radiation field, each will individually record the sig-

nals for which they were originally designed. The first will record thermal neutrons, plus electrons, plus gammas; the second, electrons and gammas, and the third gammas only. By a simple subtraction of the signal readings and a further individual calibration, the separate radiation contributions can be obtained. We must stress that the proposed entire procedure will use only a single detection technique, that is, EPR, and a single substance, *i.e.* alanine. But the implementation of this proposal requires an alanine operational neutron dosimeter.

With the aim of developing the neutron dosimeter, there is the need to perform systematic EPR measurements on neutron irradiated samples of alanine and boron crystallite mixtures. To perform this systematic analysis we must consider that the number of extra free radicals depends on two factors: the first one is the weight proportion between the two mixture components. To be precise, a mixture rich in boron crystallites will produce, when irradiated, abundant α, γ, and ^7Li projectiles, but it will have a relatively low number of alanine crystallite targets to hit, and consequently there will be a limited quantity of extra radicals produced. The second factor to consider is the size of crystallites in the alanine-boron compound mixture. Here, as a consequence of the short ranges of $\alpha-$particles, and ^7Li in solid matter, most of their deposited energy will be trapped in the bulk of the boron compound. Therefore many of the produced projectiles will not emerge from the surface of the crystallite to reach an alanine target. The exceptions are the 0.48 Mev $\gamma-$rays, most of which will escape out of the samples without even impinging on any alanine molecule and without producing extra projectiles. This due to the long range of $\gamma-$rays in the bulk as compared to those of the charged particles.

In the present work, we report the results of a series of experiments where we have systematically changed the size of the crystallites together with the boron content of the samples. These experiments point at obtaining the best EPR signal enhancement, finding the optimum combination of the two parameters (crystallite size and boron content). In addition, we present a simple model that simulates the experimental observations here submitted.

This paper is organized as follows: the following two sections will account for the experimental part of the work, while the subsequent sections will present a simple model that simulates the experimental observations. The final section discusses the results.

2. Experimental Method

The objective of this work is to measure the EPR signal intensity of several samples with different alanine to boron stoichiometric ratios and different grain sizes. The boron compound used for the experiments is borax ($Na_2B_4O_7 \cdot 10H_2O$, Baker 99.8%). This substance was selected over others, such as boric acid, because it does not react chemically with the alanine. This is a major advantage, as we shall see in our conclusions. In addition, borax does not show any EPR signal following ionizing irradiation.

TABLE I. Characteristics of the sieves, grains and standard deviations.

U.S standard number	Sieve size(mm)	Grain size (mm)	σ(mm)
No.50	0.297	1.122	0.36
No.60	0.250	0.553	0.09
No.80	0.190	0.409	0.08
No.250	0.062	0.236	0.06
No,325	0.044	0.120	0.03
Receiver pan	———	0.092	0.05

2.1. Crystallite Size

In order to keep the complexity of the experiment low, crystallites of the same size were mixed together. For this purpose borax and alanine (DL-α -alanine, Merck 99%) powders were sieved separately throughout five different testing sieves. Characteristics of the sieves used are given in Table I. All sieves meet ASTM Ell standards.

To assign a size to the crystallites retained on the sieves and in the receiver pan, we consider that crystallite size is appropriately evaluated by estimating a mean diameter "s" described as the arithmetic average of the length "l", and the width "w" of the crystallites [3]. The latter two defined as the maximum and minimum dimensions of each individual crystallite. In precise terms

$$s = \Sigma(l + w)/2n,$$

where n is the number of measured crystallites. The length l and width w of the crystallites retained in the series of sieves and in the receiver pan were determined by optical microscopy. The crystallites were spread evenly on a microscope slide, and their dimensions measured with the aid of an optical graticule. The third column of Table I shows the obtained mean diameters "s". The values shown are the arithmetic averages for the borax and alanine crystallites corresponding to the same sieve number. The fourth column, in Table I, lists the standard deviations. The reader should notice that the diameters obtained are larger than the size aperture of the corresponding sieves. This is due to the fact that the crystallites are far from having a spherical shape, so some of them pass through the grid in a tilted direction [3].

2.2. Mixtures

The alanine and borax powders, corresponding to the same sieves, *i.e.* approximately of the same crystallite size, were mixed in six different alanine:borax stoichiometric ratios for each sieve size. The mixtures were used to prepare 30 different batches of samples. Each batch is characterized by 2 parameters: its stoichiometric ratio and its crystallite size. The 30 batches correspond to the 6 possible stoichiometric ratios times the 5 crystallite sizes. Six specimens were prepared for every batch making a total of $6 \times 30 = 180$ samples. Care

was taken to keep each of them with equal alanine contents (0.04g).

An extra batch was prepared in a different form. This extra batch surged from the need to have a very small grain size. This need is justified by calculations we made of the ^7Li particles ranges in borax. They turn out to be of the order of 8.3 and 4.26 μm, respectively. We used the computer code "TRIM" to calculate these ranges [4]. These results indicate that the crystallite size of the former batches can be considered large if we contrast them with the calculated particle ranges. Therefore, we considered convenient to have samples with their mean diameter grain size smaller than those of the earlier batches.

For this purpose, 6 additional batches (of 6 samples each) were prepared by dissolving separately the 6 nominal stoichiometric mixtures in water. These solutions were then stirred thoroughly and were forced to evaporate to guarantee a fast crystallization, thus ensuring a small grain size. In this way, 6 homogeneous mixtures were achieved. By means of optical microscopy, sizes of the crystallites, as defined earlier, were found to be of around 0.02 mm.

2.3. Preparation of Samples

To eliminate possible free radicals that may appear before sample irradiation, either in the chemical product or due to the grinding of the powder mixtures, all mixtures were preheated for one hour at 100 °C.

Mixtures in powder form are difficult to handle. To ease sample handling, cylindrical pellets were manufactured (diameter = 2.9 mm, length = 30 mm) each containing each mixture and silicone as the binder. These were made using room-temperature vulcanizing silicone (RTV gel, Dow Corning). The procedure for manufacturing the pellets has been described elsewhere [5].

2.4. Neutron Irradiation

Samples were irradiated for 30 hours in the thermal column of a TRIGA Mk III nuclear reactor. The thermal neutron flux, as reported by the reactor operators was around 5×10^7 n_{th} / cm^2 s. Since γ-rays contribute to the observed EPR signal, the possibility of a γ-ray component in the column was investigated by using both alanine-silicone pellets and "Teflon" (polytetrafluoroethylene Garloc S.A.) cylinders having the same size, and placed in the same position as those occupied by the batches in the column. The same test was performed on a batch containing only borax.

Although the response of Teflon to neutrons is negligible, but it is sensitive to low levels of electron and gamma radiation. In any case, the sensitivity of alanine and Teflon to γ-rays was checked by comparing the EPR signals of samples irradiated with a standard ^{60}Co γ-irradiation source (Gammacell AECL) to those of samples placed in the thermal column. No γ-ray component was found in the thermal column using the Teflon samples. In contrast, a very faint alanine EPR signal was recorded for the alanine-only pellets. The observed signal was just above the noise level when the spectrometer was set to the highest amplifying scale. Therefore, we can consider the irradiation in the thermal column as that of a single component (i.e. thermal neutrons). But we shall see in the next section that this very faint signal of free radicals in the alanine only pellets, increases in the alanine-borax spectrum.

2.5. Spectrometer Settings

EPR measurements were performed in a Varian E 15 spectrometer following the recommendations of the ASTM Standards [1], with one exception. This was the use of a dual-resonance cavity (Varian E-232) resonating in the TE$_{104}$ mode. To compare the relative number of spins in the irradiated samples to those in the standard sample of synthetic ruby crystals, the pellet and the sample were placed each in each half of the cavity and their EPR signals recorded under the same operation conditions. The relative number of spins in each pellet can be determined accurately by comparison of the signal-height ratio between pellet and the standard.

3.   Experimental Results

A typical EPR spectrum of an irradiated sample is shown in Fig. 1. All the observed spectra in the present experiments are identical to the one observed for pure alanine.

Figure 2 shows the EPR signal intensity response curves as function of the borax contents in the samples. Each curve corresponds to one particular crystallite mean size. Each one of the 36 experimental points shown in the curves was obtained by averaging the signal response of each one of the samples corresponding to one particular boron concentration and crystalline size. The curves, joining the experimental points shown in the figure were created by fitting a polynomial to the data.
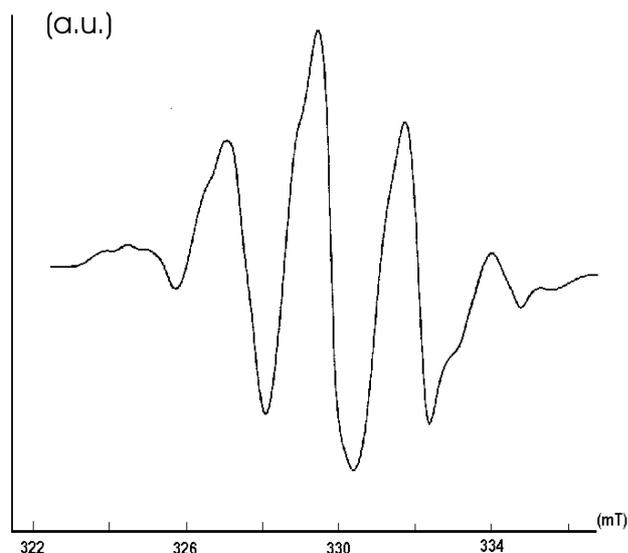

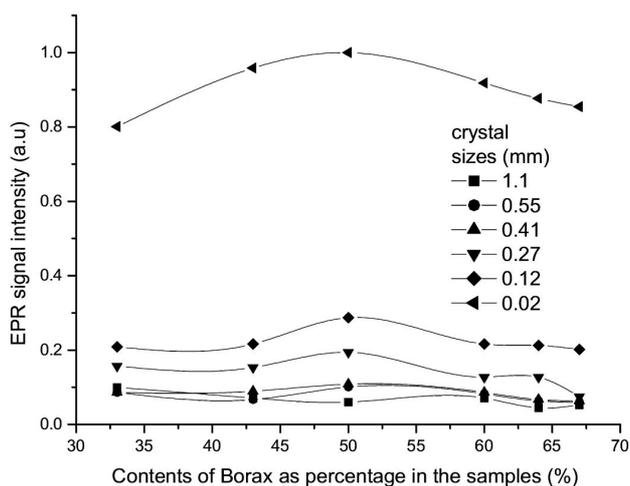FIGURE 1. Typical EPR spectrum of an alanine-borax mixture

FIGURE 2. EPR signal intensity as function of borax contents.

FIGURE 3. EPR signal versus crystallite size for a 1:1 alanine borax ratio.

Three remarks can be said about the results shown in Fig. 2: i) The curves indicate, as expected, that the smaller the grain size, the larger the EPR signal response curve, ii) the best signal response corresponds to a 1:1 alanine:borax stoichiometric ratio, (*i.e.* 50% of borax), and iii) for the larger grain sizes, the response curves crisscross. This may be due to a partial orientation effect of the crystal grains. We observed a signal intensity response variation for those samples with larger crystallites, when rotating the pellets around the vertical mid-axis of the cavity. This orientation effect has already been reported by other authors and can be considered primarily due to alignment of bigger single crystallites among smaller ones [6]. Reports claim that this effect has produced variations of up to 10-15 % with rotation of the sample around the mid-axis in the cavity while held within the quartz sample tube. The effect is reduced with smaller crystallites [6].

The enhancement observed from the most intense signal with respect to the signal of the alanine, only pellets turns out to be 12.3-fold. This, as already pointed, corresponds to the batch formed with the smaller crystallites and a stoichiometric ratio of 1:1.

In the next section, we shall present a very simple model on the behavior of the response curves.

4. A Simple Model

We have already proposed that the number of free radicals created in the alanine, and consequently the intensity of the EPR signals, depends on two factors: Namely, the size of crystallites in the alanine-borax mixture, and the stoichiometric proportion between the two mixture components. In the first case, many of the produced projectiles in the volume will not emerge from the surface of the crystallite to reach an alanine target. It is clear then, that this will depend on the surface to volume ratio of the borax crystals. In order to test this simple hypothesis, Fig. 3 shows the EPR signal intensity as function of the crystallite size for the 1:1 alanine-borax ratio.
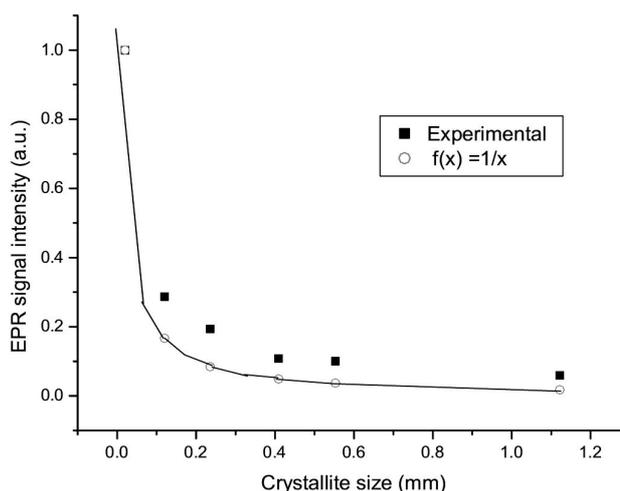
It is seen from the figure that the $1/s$ variation fits fairly well the experimental data.

As for the second factor, that is, the proportion between the two mixture components, it is apparent that we are on a "predator-prey" situation. So let us begin by writing a conservation equation,

$$N_A + N_B = 1, \tag{2}$$

where N_A and N_B are the proportions of alanine and borax in a sample, respectively.

The number of free radicals produced in the sample is a function of the number of projectiles produced on irradiation, which in turn is proportional to the borax contents of the samples. On the other hand, the production of radicals is also proportional to the number of alanine targets. Since both factors are independent, it is then valid to state that the number of free radicals is proportional to the product of the two factors, that is

$$\text{EPR signal intensity} = N_A N_B, \tag{3}$$

where we have and assumed a linear proportionality relation, and we excluded the proportionality constant.

Making use of the conservation equation we may write

$$\text{EPR signal intensity} = N_B(1 - N_B), \tag{4}$$

which is a sort of "logistic" relation.

Figure 4 shows a comparison between the above relation and the experimental data for the smaller size crystallites (0.02 mm).
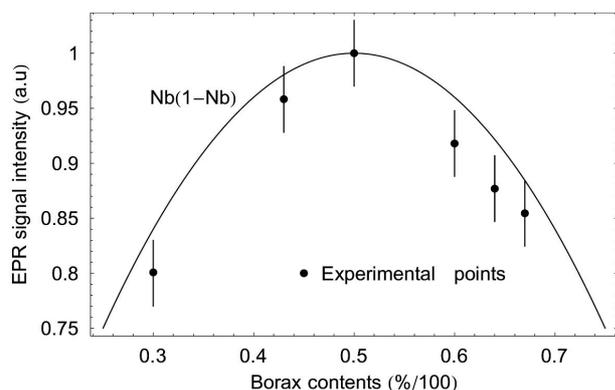
FIGURE 4. Comparison between a logistic growth relation and the EPR signal intensity for a 1:1 stoiquiometric relation for the smaller size crystallites.

5. Conclusion

Concerning the EPR signal intensity variation with the borax contents, a visual inspection of Fig. 4 shows that the simple model here presented follows the trait of the experimental points. Nevertheless, the model predicts higher EPR response values than those experimentally obtained. The reason for this can lie in the model itself, as it does not take into account the silicone binder role. The binder will trap some of the projectiles preventing them to reach alanine crystallites consequently diminishing the signal intensity.

In the case of the EPR signal intensity variation with the crystallite size, we observe from Fig. 3 that the theoretical curve follows the trait of the experimental data. However, it does not fall within the domains of the error bars. To be precise, the model is consistently predicting a lower EPR signal intensity response. This difference could be attributed to measurement errors and approximations of the model. We consider that the major source of error rests in the measurement of the crystallite size. Due to the many irregularities in the shapes of the crystallites, they tend to rest on the microscope slide in their most stable position, and this contributes to a measurement bias. This, in turn, would mean that we are consistently obtaining larger values for the grain sizes. If this were the case, then the experimental points shown in Fig. 3 should be shifted towards the lower grain size values, and it is clear from the same figure that the differences between experimental and predicted values would decrease.

In both situations, the proposed model, although schematic, is adequate to explain the experimental data trends. However the model cannot be used to accurately forecast results for the experiments at larger grain sizes. At most, it can predict for these latter situations, the point of maximum EPR signal intensity.

Finally, we must remark that the best signal response was obtained for a grain size of around 0.02 mm and for a stoichiometric 1:1 relation (see Fig. 2). Efforts concerning the production of thermal neutron dosimeters should therefore center on this ratio, with crystallites of this dimension or smaller.

However, we would like to mention that in a previous paper the variation of the EPR signal intensity of neutron - irradiated alanine and boric acid was measured as function of the boric acid contents in the sample [2]. In those earlier experiments, it was found that the maximum signal was obtained as in this work, for those samples that were prepared by dissolving the boric acid in water together with the alanine and afterwards forcing the solution to dry. The data shown in that previous work demonstrates that the optimum signal is obtained for the smaller crystallites and a stoichiometric ratio of 1:1.5. This raises an essential question on why the ratio is not 1:1, as in the present work.

A likely answer is that for the former boric acid experiment, we are in the presence of a 3 ingredient system, namely: boric acid, alanine and alanine hydroboride. As investigated in a previous work, boric acid and alanine when added to water might transform part of the salt into a boride [7]. This implies considering a more complicated model involving a "predator" and two different types of "prey" (alanine and its boride). Consequently, we face the problem of the boride creation which depends on the chemical reaction of the salt and the acid. To finish up this point, the former system is different to the present one, so it should be explained by modifying our oversimplified model.

However, returning to the earlier suggestion of using boric acid, findings have been reported where alanine hydroboride has been used as a dosimetric substance [7, 8]. These reports indicate that the signal enhancement of the EPR signal is greater that the one reported in this work. Namely the signal improvement was increased 27.3 fold over alanine alone [7]. This value contrasts advantageously with the one of 12.3-fold, found in this work for the borax-alanine mixtures. However, the advantage of the present proposal of using borax for a dosimetric system instead of using hydroboride, lays in the fact that the former does not involve a chemical reaction control, whereas the latter does. As reported earlier, the EPR signal enhancement for the hydroboride case depends heavily on the preparation method, whether is in an alkaline, neutral or acidic media [8]. On the contrary, the present work requires only the mixing of substances that do not react between them. Nevertheless, a delicate point in the present technique is that the dosimeters require good homogeneity on the mixtures and on the mean crystallite size if one wishes a reasonable sensitivity. Otherwise an appreciable random uncertainty is introduced. Another point that deserves further investigation is the dosimeter response to the thermal neutron energy spectrum. Because of the 1/E form of the cross section for neutron capture in boron, the dosimeter response depends on the energy spectrum. This might limit this technique to be used in analogous thermal neutron environments. Future experiments will aim at establishing a thermal dosimetric technique based on the work presented here.

Acknowledgments

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