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ELECTRON PARAMAGNETIC RESONANCE OF HYDROGEN
CENTERS IN NATURAL BERYL

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INTRODUCTION

X-ray (Koryagin and Grechushnikov, 1966; Bershov, 1970) and UV-irradiated (Blak et al., 1982) beryl shows the presence of atomic hydrogen and methyl radicals, stable at room temperature. These centers are not observed if beryl is completely dehydrated (Koryagin and Grechushnikov, 1966). Both H° and CH_3 were assigned to sites in the channels and were assumed to arise from radiation-induced decomposition of water and methane molecules. It was observed that H° is unstable above $200^{\circ}C$ (Edgar and Vance, 1977). In this paper, isothermal decay of the EPR line of the atomic hydrogen in beryl produced by UV irradiation, is reported. The g and A parameters are also determined.

ABSTRACT

An EPR study of the decay kinetics of atomic hydrogen centers in beryl is reported. The measured spin Hamiltonian parameters are: $g = 2.0054 \pm 0.0003$ and $A = (0.930 \pm 0.002) \cdot 10^{-17}$ erg. The isothermal annealing was measured for temperatures ranging from 60° to $180^{\circ}C$.

EXPERIMENTAL METHODS

Natural colorless beryl of near gem-quality from the Claire Azadian collection from Minas Gerais, Brazil, was studied. Slices of $2 \times 2 \times (5-10)$ mm were cut. The EPR measurements were done using an X-band homodyne reflection-type spectrometer assembled with separate units from Varian Associates and Micro-Now Instrument Co., Inc.. The temperature was controlled with a model V-4540 Varian unit and measured with a chromel-alumel thermocouple located at about 1 mm above the sample. The hydrogen centers were produced by UV-irradiation of the samples at room temperature with a 400W Hg lamp.

A series of measurements was carried out to

obtain the isothermal annealing of the H° centers in beryl. The isothermal decay was produced inside the EPR spectrometer with heated nitrogen gas flowing directly onto the sample. The EPR signal from the high-field H° line was measured at regular intervals of time with the temperature held constant at T_1 . After the measurements at T_1 were finished, the sample was annealed at 400°C for 1h in order to assure identical conditions before each new UV-irradiation. The second series of measurements was done at a constant temperature T_2 , and so on.

RESULTS AND DISCUSSION

The EPR spectrum of UV irradiated beryl (Fig.1) shows the well known doublet of atomic hydrogen located at $H_1 = (0.2947 \pm 0.0003)\text{T}$ and $H_2 = (0.3450 \pm 0.0003)\text{T}$ measured at the microwave frequency of $9.0326 \cdot 10^9\text{Hz}$. The magnetic field was measured with a Varian NMR gaussmeter. The

Insert Fig. 1

spectrum can be interpreted with the spin Hamiltonian:

$$\underline{H}(S) = g\beta \underline{H} \cdot \underline{S} + g_n \beta_n \underline{H} \cdot \underline{I} + A \underline{S} \cdot \underline{I}, \quad (1)$$

where the first term is the isotropic electronic Zeeman interaction with the applied magnetic field, the second is the nuclear Zeeman interaction with the external field and the third is

the isotropic hyperfine interaction between the unpaired electron and the proton magnetic moment.

After diagonalizing this spin Hamiltonian in the four-dimensional $S = 1/2, I = 1/2$ vector space, the two $\Delta M_S = \pm 1, \Delta M_I = 0$ transition energies arise as follows:

$$h\nu = \frac{A}{2} + \frac{1}{2}(g\beta - g_n\beta_n)H_1 + \frac{1}{2}[(g\beta + g_n\beta_n)^2 H_1^2 + A^2]^{1/2}, \quad (2)$$

and

$$h\nu = -\frac{A}{2} + \frac{1}{2}(g\beta - g_n\beta_n)H_2 + \frac{1}{2}[(g\beta + g_n\beta_n)^2 H_2^2 + A^2]^{1/2} \quad (3)$$

A few straightforward calculations give the following relations for the spectroscopic splitting g factor and the hyperfine constant A (Camargo, 1985):

$$A = \pm \frac{h\nu - (g\beta - g_n\beta_n)H_{1,2} - g\beta g_n\beta_n H_{1,2}^2 / h\nu}{1 - (g\beta - g_n\beta_n)H_{1,2} / 2h\nu}, \quad (4)$$

and

$$g = \frac{(1 \mp A/h\nu)h\nu + (1 \mp A/2h\nu)g_n\beta_n H_{1,2}}{[(1 \mp A/2h\nu) + g_n\beta_n H_{1,2}/h\nu]\beta H_{1,2}}, \quad (5)$$

where the constants have the usual meaning, the upper sign corresponds to H_1 and the lower one to H_2 . Both calculations should yield coincident values for g and A .

Applying this method to the above experimental data we get $g = 2.0054 \pm 0.0003$ and $A = (0.930 \pm 0.002) \cdot 10^{-17}\text{erg}$ after a few iterations. The small g -shift $\Delta g = 0.003$ indicates that H° is almost free from interactions in the trap. The electron spin density at the nucleus of the H° center in beryl is slightly smaller than in the free hydrogen atom, since we have $\delta A/A_{\text{free}} = -1\%$. Assuming Adrian's calculations (Adrian, 1960) of

the matrix effects on the EPR spectra of hydrogen atoms stabilized in nonpolar matrices also valid for beryl, it must be concluded that the van der Waals attractive interaction is stronger than the repulsive Pauli exclusion forces. It is well known that these interactions contribute to the hyperfine constant with opposite sign.

Fig. 2 shows the isothermal decay kinetics of the EPR signal for the H° center in beryl at 60° , 80° , 100° ,

Insert Fig. 2

120° , 140° , 160° and $180^{\circ}C$, respectively, in a semilogarithmic scale. The intensity of the EPR signal has reduced by one-half after about 15 min. at $120^{\circ}C$. This fast decay is followed by a slower one. The behavior of the slower part of the decay was analysed in terms of the first and second order processes (Curie, 1963).

In the first order process, the decrease of the concentration n of H° centers is described by

$$\frac{dn}{dt} = -\alpha n, \quad (6)$$

where t is the heating time and α , the rate constant, is an adjustable parameter. The α parameter is expected to obey Arrhenius' law. The solution of the above equation is

$$n^I = n_0 e^{-\alpha t}, \quad (7)$$

where n_0 is the initial concentration of H° .

In the second order process the decrease of the concentration n is given by

$$\frac{dn}{dt} = -\alpha n^2 \quad (8)$$

Here also, the α parameter is expected to obey Arrhenius law. The solution of the above equation gives:

$$n^{II} = n_0 / (1 + \alpha n_0 t). \quad (9)$$

Fig. 3 shows the relation between α vs $1/T$ for first

Insert Fig. 3

and second order processes in semilogarithmic scale. The behavior for both processes does not obey the Arrhenius law.

Kayser and Hubbard, 1983, proposed a model considering situations in which particles diffuse in a d -dimensional space with random distribution of stationary traps. The density of particles was assumed to follow the $\exp(-t^{d/d+2})$ law. The H_i° thermal decay could not be satisfactorily adjusted for $d=1, 2$ or 3 .

The successive attempts to adjust the experimental data to a sole kinetic process led to the conclusion that H_i° thermal decay in natural beryl involves at least two or more distinct processes.

A method of data processing, based on the U_{2x} center model, is presently being developed by assuming a system of differential kinetic equations for all possible reactions which can occur in the decay process. The results will be published in the near future.

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FIGURE CAPTIONS

- FIGURE 1. Electron paramagnetic resonance spectrum of colorless beryl showing the appearance of the H^0 lines.
- FIGURE 2. Isothermal decay of the electron paramagnetic resonance signal of the H^0 center at 60° , 80° , 100° , 120° , 140° , 160° and 180°C , respectively, in a semilogarithmic scale.
- FIGURE 3. Relation between the α parameters of equations (6) and (8) versus T^{-1} in semilogarithmic scale.

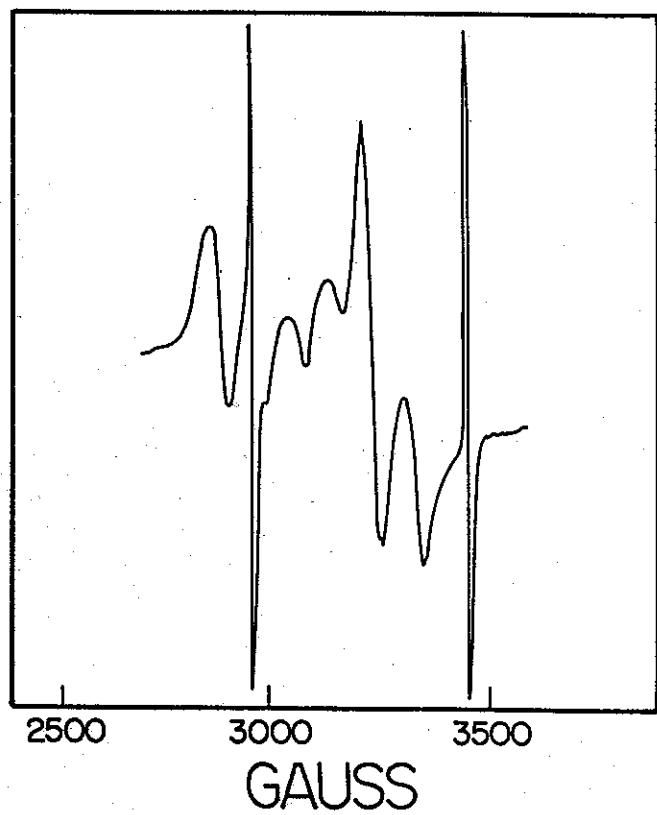


FIGURE 1

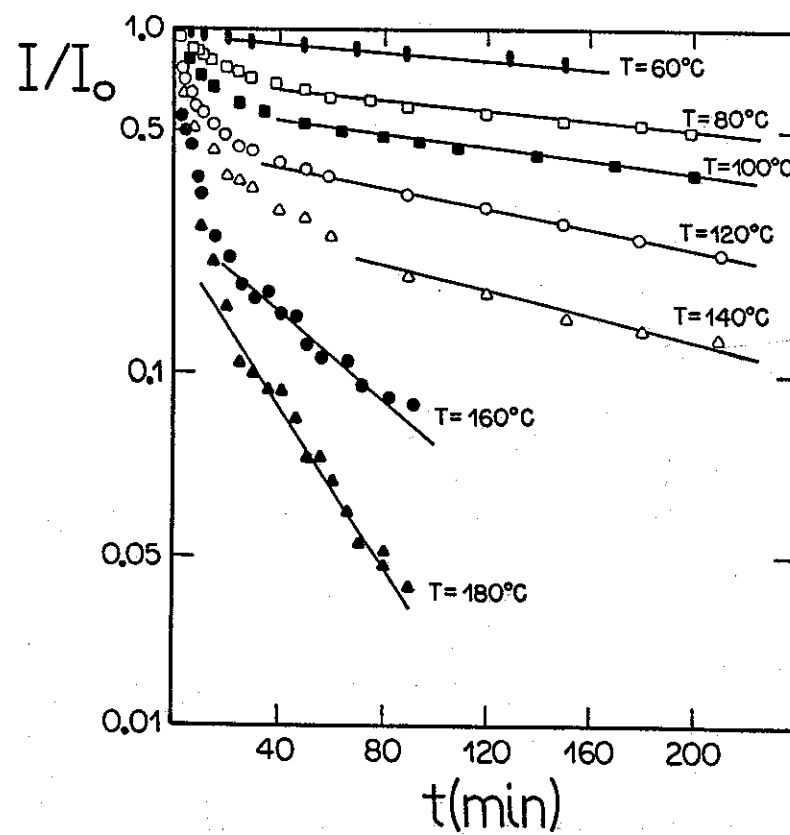


FIGURE 2

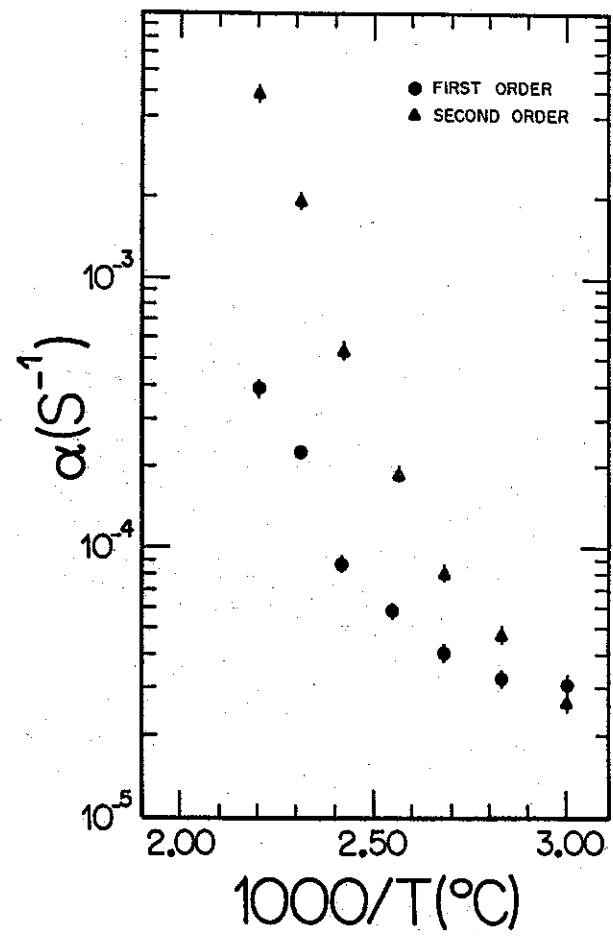


FIGURE 3