

Electron Paramagnetic Resonance of Atomic Hydrogen Centers in Rubellite

(rubellite|hydrogen|annealing kinetics|EPR)

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INTRODUCTION

Atomic hydrogen stabilized in solids is potentially a valuable tool in order to obtain physical insight based on the knowledge of the simplest possible paramagnet. Several electron paramagnetic resonance (EPR) studies of atomic hydrogen trapped at various kinds of sites in different materials are available in the literature (Bessent *et al.*, 1967; Foner *et al.*, 1960; Hall and Schumaker, 1962; Helbert and Kevan, 1973; Jen *et al.*, 1958; Koryagin and Grechushnikov, 1966; Livingston *et al.*, 1955; Perlson and Weil, 1974; Pontuschka *et al.*, 1982; Pontuschka *et al.*, 1982; Smith, 1964; Weeks and Abraham, 1965), but very little is known about the processes dealing with the stability of this very reactive species in solids.

In the present we report a new atomic hydrogen center, U_R , observed in rubellite (pink tourmaline) γ -irradiated at room temperature with EPR measurements. These measurements provided the experimental support for the model we have developed in order to explain the high stability of atomic hydrogen in this material.

The spatial symmetry group of tourmaline is $R3m$ and the unit cell parameters are $a = 15.84 - 16.03 \text{ \AA}$ and $c = 7.10 - 7.25 \text{ \AA}$. The structure, as described by Godovikov, 1975, is shown in Figure 1 where (a) is the structure of antigorite, which is composed by

the structure of brucite (three octahedra centered by the cations Li^+ , Mn^{++} , Mn^{+++} , Fe^{++} or Fe^{+++} distributed at random throughout the volume of the crystal, forming a solid solution) and the hexagonal ring of SiO_4 tetrahedra; (b) is brucite bonded with $AlO_5(OH)$ octahedra and (c) shows the helicoidal chain of antigorites linked together by means of $AlO_5(OH)$ octahedral units.

EXPERIMENTAL METHODS

Natural rubellite (pink tourmaline) from Minas Gerais, Brazil, of gem-quality was studied. Slices of $2 \times 2 \times (5 \sim 10)$ mm were cut.

Three EPR measurements were done using a X-band homodyne reflection-type spectrometer assembled with units made by Varian Associates and Micro-Now Instruments Co., Inc. The temperature was controlled with model V-4540 unit made by Varian Associates and measured with a chromel-alumel thermocouple located at about 1 mm above the sample.

The samples were γ -irradiated at room temperature with ^{60}Co γ -rays in the source of the EMBRARAD S.A. at doses of about 500 KGy.

A series of measurements was carried out to obtain the isothermal annealing of the H^0 centers in rubellite using the following pro-

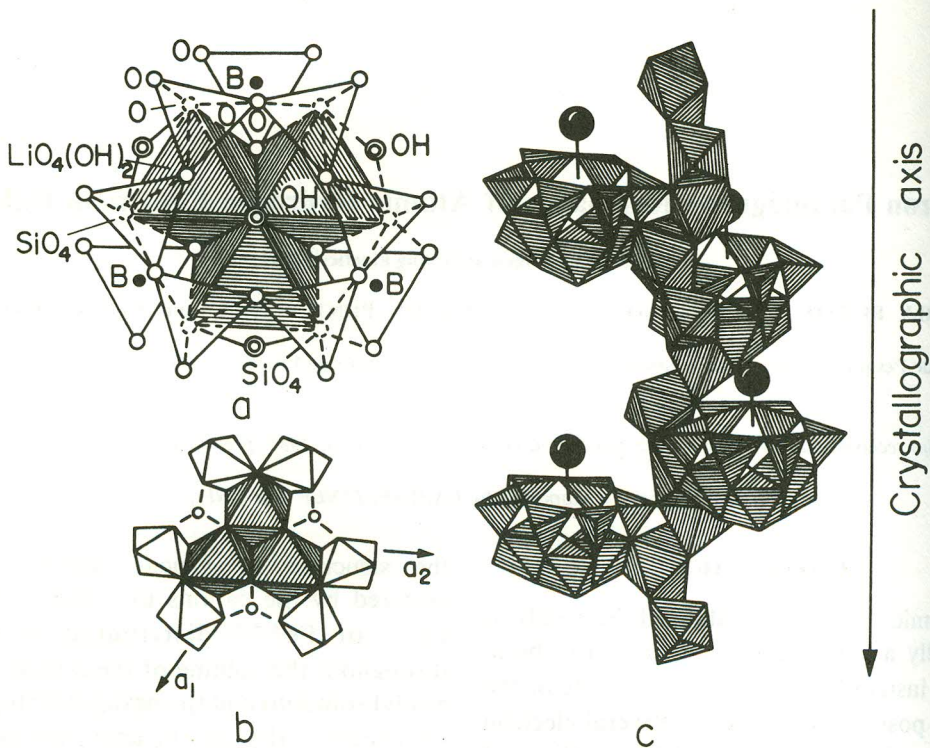


Fig. 1 — The structure of tourmaline, after Godovikov, 1975. (a) Structural grouping of antigorite, consisted of a brucite group at the bottom (three octahedra of $\text{LiO}_4(\text{OH})_2$ and planar BO_3 units) and hexagonal silicate ring at the top. (b) Bottom view of the brucite with $\text{AlO}_5(\text{OH})$ octahedra. (c) Helicoidal chain of antigorite groupings connected by means of $\text{AlO}_5(\text{OH})$ octahedra.

cedure: nitrogen heated at temperature T_1 is injected in a quartz tube inserted in the EPR cavity. The sample was put in the quartz tube and the H^0 EPR signal was recorded from time to time. After a series of measurements at T_1 was completed, the sample was annealed at 400°C for 8 ~ 10 h and γ -irradiated again. The process was repeated at a second temperature T_2 and so on.

The isochronal heat treatment was done directly in the EPR resonant cavity: the sample was heated to temperature T_1 , held for 10 min., lowered to 303K for EPR measurement, raised to a higher temperature $T_2 > T_1$, held for 10 min., lowered again to 303K for EPR measurement, etc.

RESULTS

The analysis of the well known H^0 doublet signal shown in Figura 2 provided the evaluation of the spin Hamiltonian

parameters $g = 2.0052 \pm 0.003$ and $A = (9.31 \pm 0.02) \cdot 10^{-18}$ erg, where g is the factor of the Zeeman interaction of the paramagnetic electron spin with the external magnetic field and A is the hyperfine structure constant, which is a measure of the electron spin density

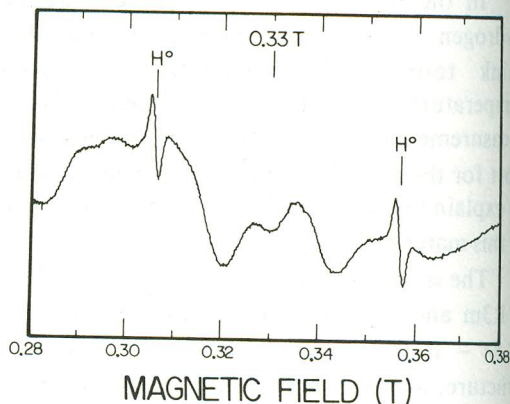


Fig. 2 — Electron paramagnetic resonance spectrum of rubellite showing the appearance of the H^0 lines.

at the site of the atomic hydrogen nucleus. The positive g -shift $\Delta g = 0.0029$, as compared with the g -value of the free electron, is an effect of spin-orbit interaction and the relative A shift $\delta A/A$ compared with corresponding value for the free atomic hydrogen shall be discussed below.

The line-width of 15 Oe has remained constant at temperatures ranging from 4.2 to 265K leading to the result that the atomic hydrogen does not diffuse throughout the rubellite structure. The line-shape was essentially Gaussian, inhomogeneously broadened probably due to dipole-dipole interactions between the magnetic moments of atomic hydrogen and the ions (Li^+ , Mn^{2+} , Mn^{3+} , Fe^{2+} , Fe^{3+}) randomly distributed among the brucite structure octahedral sites. The randomness of this solid solution of metallic ions is probably the reason of the isotropy observed of the H^0 EPR spec-

trum. The γ -irradiation of the samples did not produce appreciable changes in the complex remaining EPR spectrum which could eventually suggest significant changes of the relative concentrations of oxidation state of Fe^{2+} ions or another transition metal ion.

Isothermal annealing experiments of atomic hydrogen EPR spectra were carried out at different temperatures (Fig. 3). After an initial rapid decay in which the temperature of the sample reaches the equilibrium, when $\sim 20\%$ of hydrogen was recombined, the further annealing obeyed first order kinetics. This has the meaning that the trapped atoms recombine immediately as soon as they overcome the potential barrier, which is in agreement that the hydrogen cannot diffuse through the material. Following Arrhenius, the activation energy was found to be $E = (1.1 \pm 0.1)$ eV. To our knowledge, this value is among the highest

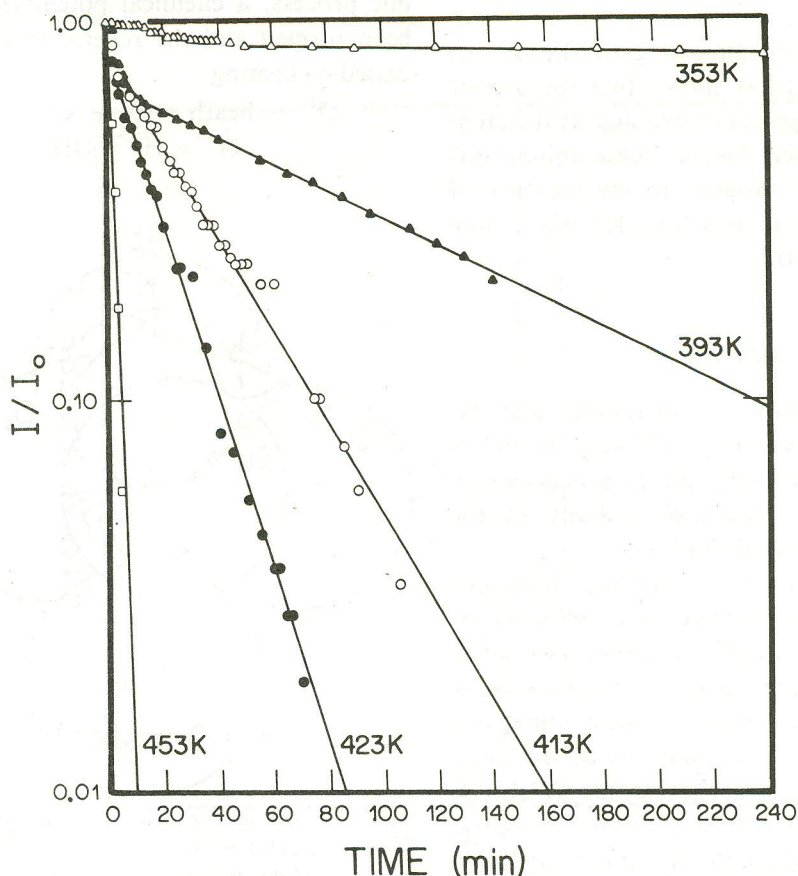


Fig. 3 — Isochronal decay of the U_R center in rubellite γ -irradiated with Co^{60} source. The experimental data were normalized to the initial intensities.

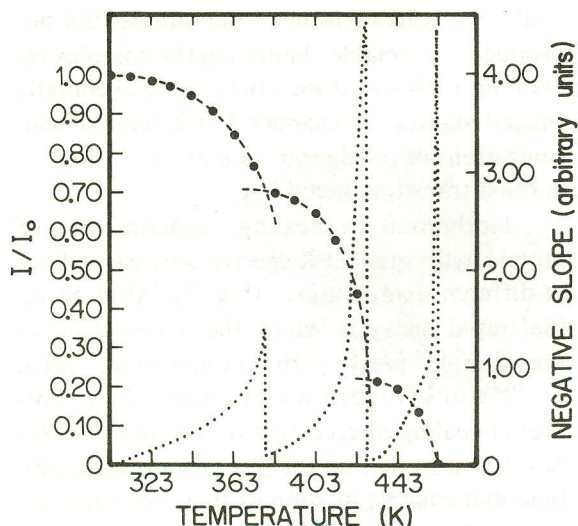


Fig. 4 — Isochronal decay of the U_R center in rubellite γ -irradiated with Co^{60} source. The negative derivative curve was constructed from the curve drawn from the experimental results.

already reported for atomic hydrogen trapped in solids.

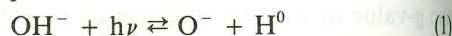
The isochronal annealing of the atomic hydrogen (Fig. 4) has shown that the atomic hydrogen was trapped in three slightly different sites. As explained below, these minor differences could be assigned to the presence of three different alkali ions Na^+ , K^+ , Rb^+ , close to the hydrogen site.

DISCUSSION

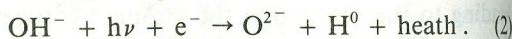
From structural considerations and experimental observations, following model is proposed in order to explain the process which is responsible for the high stability of the atomic hydrogen in rubellite.

The appearance of atomic hydrogen through radiation damage in rubellite is attributed to the hydroxyl radiolysis. Two kinds of hydroxyls are present in the structure: those located at the inner side and those on outer side of the antigorite. The radiolysis of the outer hydroxyls releases hydrogen atoms which diffuse and recombine freely, without stabilization. Notwithstanding, the inner hydroxyl releases hydrogen which is confined inside a cage and recombines again repeatedly under

the effects of γ -irradiation, following the reversible equation:



Now, if it happens at some instance, that an electron released e.g. from oxidizing reactions of Mn^{++} or Fe^{++} ion, located at the center of a brucite octahedron, reaches the O^- ion during its short life time, the following reaction takes place:



Since the outer shell of O^{2-} is complete, this is actually a stabilization reaction for the hydrogen center. The confining cage is limited longitudinally by the O^{2-} and Na^+ ions and perpendicularly by the inner oxygens of the hexagonal silicate ring (Fig. 5). The atomic hydrogen stabilized in this cage, found in pink tourmaline (rubellite), shall be subsequently referred to as U_R center.

As the expression (2) represents an exothermic process, a chemical potential barrier has been formed and the reverse reaction is processed on heating:

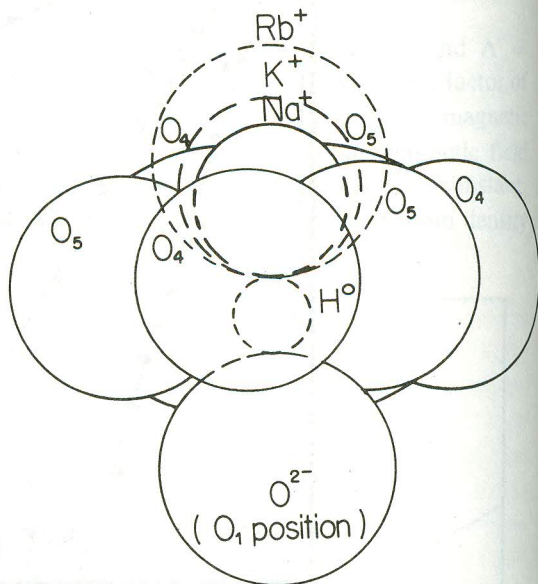
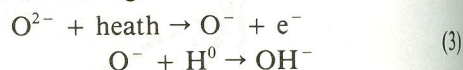


Fig. 5 — Stabilizing site of the U_R center γ -irradiated rubellite. The O_4 and O_5 oxygens are the inner corners of the SiO_4 tetrahedra of the ring structure. The O^{2-} ion is at the position O_1 , the common vertex of the three brucite octahedra units. The ionic radii are shown on scale.

Therefore, the barrier height should be approximately equal to the 1st order decay kinetics activation energy, equal to $(1.1 \cdot 0.1)$ eV, from our isothermal annealing measurements, which corresponds in this model to the O^{2-} ionization energy at this site (Fig. 6).

The differences in ionic radii of the alkali ions Na^+ , K^+ and Rb^+ in the neighbourhood of the U_R center produce different lengths of the shallow potential well. These differences affect slightly the collision frequency of the U_R center against the potential barrier between hydrogen and O^{2-} ion. When this length is shorter, the number of collisions per second is increased and center decays at slightly lower temperature. Otherwise, for longer lengths the corresponding decay occurs at slightly higher temperatures. The three steps of isochronal decay of U_R center in rubellite, enhanced by the negative derivative curve shown in Figure 4, are attributed to U_R sites having Na^+ , K^+ and Rb^+ ions, respectively.

The observed positive g-shift can be explained on the basis of the polarization of the U_R center by the strong electric field produced mainly by the closer O^{2-} and Na^+ ions. This produces the arising of effective holes in the 1s hydrogen orbital hybridized with excited states. Consequently, the spin-orbit interaction with the overlapping closed O^{2-} external shell has negative sign, yielding an increased value of

$$g = g_c - c\lambda/\Delta E$$

where g_c = free electron g-factor, c = positive constant (2nd order perturbation), λ = spin-orbit interaction constant, $\Delta E = 10.2$ eV (difference between the hydrogen 1st excited and the ground state).

The negative shift of the hfs constant, $\delta A/A = -0.001$, can be explained in terms of the combined effects of local electric field and van der Waals attractive interaction (Adrian, 1960), which is stronger than repulsive Pauli exclusion force interaction.

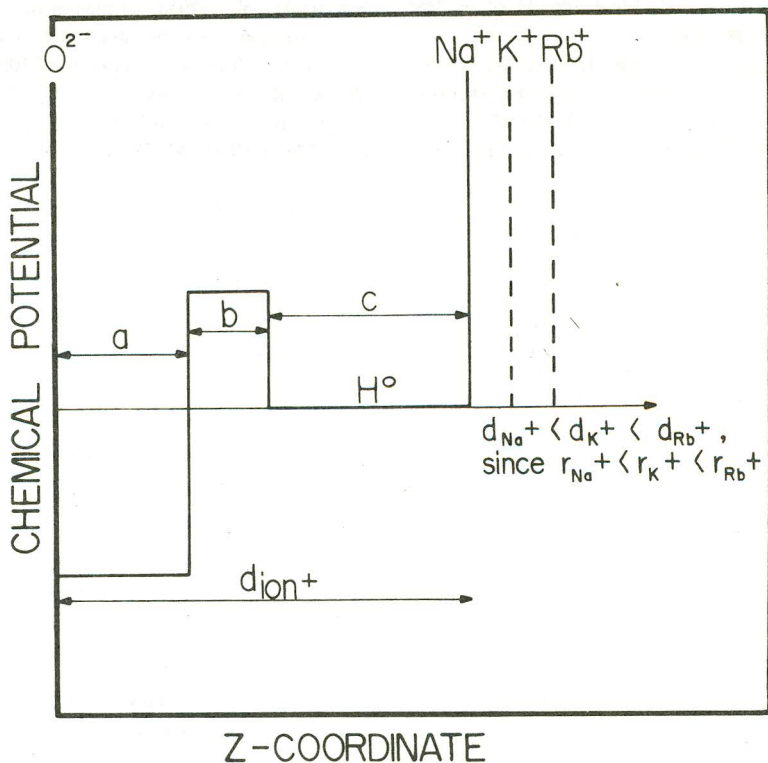


Fig. 6 — Qualitative sketch of the chemical potential seen by the atomic hydrogen in tourmaline. The small changes in length c of the shallow potential well are attributed to the different ionic radii of the alkali ions Na^+ , K^+ and Rb^+ .

A detailed analysis of this model of U_R center is in progress.

SUMMARY

EPR measurements have been used to the study of a new atomic hydrogen center, U_R , in γ -irradiated rubellite. It is proposed a model in order to explain the process of stabilization of the atomic hydrogen. Isochronal and isothermal annealing kinetics measurements have been performed. It was observed that the recombination follows Arrhenius function and the kinetics is of first order, with activation energy $E = (1.1 \pm 0.1)$ eV. The behavior of U_R EPR line intensity at low temperatures was explained in the framework of the proposed model.

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