Atomic Hydrogen in the Mineral Brasilianite $NaAl_3(PO_4)_2(OH)_4$

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EPR parameters for atomic hydrogen in three nonequivalent special positions at the twofold axis of the monoclinic structure of brazilianite, formed by X-ray irradiation at room temperature, are reported. The *g*-factors are practically isotropic and close to the free electron value, but the hyperfine splittings exhibit considerable anisotropy. One of the centers shows an additional doublet splitting, most likely due to hyperfine interaction with the proton of one of the OH groups. These hydrogen atoms have the highest thermal stability yet reported. With repeated thermal destruction and formation by ionizing radiation one of the centers is rapidly depleted. Thus they must be formed at defect sites, not from the undisturbed OH groups, and trapped near the sites of formation and their thermal destruction must at least in part be irreversible. Possible defects for their formation are discussed.

Introduction

Formation of atomic hydrogen with ionizing irradiation has been observed in a number of crystalline matrices including CaF_2 [1, 2], alkali halides [3, 4], quartz [5–7], beryl [8] and some phosphates [9, 10]. In many systems they can only be observed at low temperatures, but in CaF_2 and in the phosphates they are stable up to temperatures in the range of 100 °C. Trapping at the basic anions was thought to be responsible for this high stability in the latter compounds [9]. This explanation does not hold for CaF_2, and generally speaking the depth of the traps determines their stability. In the majority of these cases hydrogen atoms must be formed from defects since the pure crystals do not contain any hydrogen. A plausible mechanism for their formation in phosphates and compounds of other multivalent anions is a partial formation of the more acidic compounds by replacement of cations by hydrogen in the form of OH groups. The hydrogen could then be trapped at vacant cation sites in case of this type of disorder.

The mineral brazilianite is particularly suited to check this possibility for two reasons:

1. Like in the case of α-quartz [7] the low site symmetry of the crystal should allow an unambiguous identification of the trapping sites through comparison of the directions of the principal axes for the EPR parameters with bond directions in the crystal.
2. It contains hydrogen in stoichiometric amounts, and atomic hydrogen might be formed either from this stoichiometric content or from additional hydrogen present as defects. In the latter case repeated thermal destruction and re-irradiation should lead to depletion of hydrogen if the original defects are not completely restored thermally.

At least partial answers to these interrelated questions were obtained for this system.

Crystal Structure of Brazilianite

The crystal structure of brazilianite was determined by Gatehouse and Miskin [11]. The mineral crystallizes with the monoclinic space group $P2_1/b$ and four formula units per unit cell. All atoms are situated on general positions. The four OH groups are bonded to six-coordinated aluminium ions, but are not constituents of the PO_4 groups.

Results and Discussion

Formation and EPR Spectra of Hydrogen Centers

Light green crystals of brazilianite were obtained from Minas Geraes, Brazil. Although these crystals contained a number of radiation defects like hole centers on oxygen adjacent to both aluminum and phosphorus [12], no atomic hydrogen was present initially. It was, however, readily formed by X-ray irradiation at room temperature after thermal destruction of the original radiation defects (and the green color originating from divalent iron). Atomic hydrogen is formed at three magnetically nonequivalent sites, as can be seen from Figure 1. All three centers exhibit considerable anisotropy of their hyperfine splittings, and these attain extrema for the magnetic field aligned along the *b*-axis of

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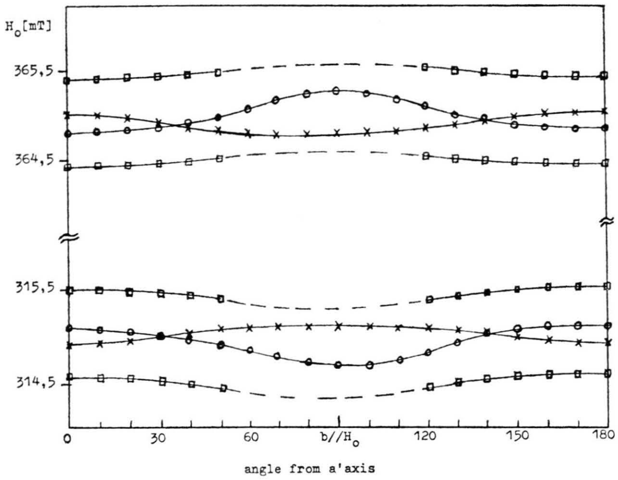


Fig. 1. Angular variation of the EPR spectra of hydrogen atom centers for rotation around the *c*-axis of brazilianite at room temperature. Microwave frequency 9.595 GHz; ○, × and □ centers A, B and C resp.

the crystal. Hydrogen must therefore be located in three of the four special C_i positions on this axis. One of the centers shows an additional doublet splitting with separations between 1.0 and 1.2 mT. Due to considerable overlap of the three spectra with linewidths near 0.3 mT this splitting was not resolved at all orientations. This fairly large linewidth is most likely due to unresolved hyperfine splittings from neighboring ^{27}Al, ^{31}P, ^{1}H and ^{23}Na nuclei. The hyperfine coupling tensors and their principal directions were determined from the data in Fig. 1 and an additional rotation around the *c*-axis. They are listed in Table 1. The *g*-factors are almost isotropic and close to the free electron value. The *g*-factors between 2.0019 and 2.0025 are in the range of those observed for most of the hydrogen atoms in other matrices, and the maximum angular variations of about 0.0002 are similar to that in α-quartz [7]. The anisotropy of the hyperfine splittings is considerable, both lower and higher splittings than for atomic hydrogen in free space (50,684 mT [13]) are observed. This variation reflects the sizes of the C_i sites with larger hyperfine splittings in the directions of compression and smaller splittings in the regions of dilatation. The additional hyperfine splitting of center C could arise from interaction with either a ^{31}P nucleus or a proton of an OH group. Since the phosphorus atoms are well shielded by their oxygen tetrahedra, interaction with an additional proton is more likely. From the size of the isotropic part of this splitting a distance of about 0.10 nm between hydrogen atom C and this proton is calculated. This value is larger than the bond distance in the H_2 molecule of 0.074 nm and the crystal radius of a proton of 0.025 nm, but smaller than the van der Waals radius of a proton of 0.14 nm [14].

Table 1. EPR parameters for the atomic hydrogen centers in brazilianite.

Center	Hyperfine coupling constants [MHz]	Directional cosines [a]		
A	$A_1 = 1455$	1.000	0.000	0.000
	$A_2 = 1447$	0.000	− 0.701	0.713
	$A_3 = 1369$	0.000	0.713	0.701
B	$A_1 = 1415$	1.000	0.000	0.000
	$A_2 = 1405$	0.000	− 0.267	0.964
	$A_3 = 1373$	0.000	0.964	0.267
C	$A_1 = 1433$	1.000	0.000	0.000
	$A_2 = 1408$	0.000	− 0.595	0.804
	$A_3 = 1382$	0.000	0.804	0.595
	$A_1' = 27.6$	1.000	0.000	0.000
	$A_2' = 29.0$	0.000	− 0.139	0.990
	$A_3' = 33.6$	0.000	0.990	0.139

[a] Components along the axes *b*, *c* and *a'* (— 7.4° from the *a*-axis of the crystal).

All three centers are stable at temperatures below 150 °C. They decay at comparable rates at higher temperatures. This is the highest thermal stability yet reported for atomic hydrogen in any solid. A broad optical absorption band at 41900 cm^{-1} correlates well with the intensities of the hydrogen EPR spectra. It has practically the same position as the corresponding 1 s → 2 p transition of hydrogen in KCl [15].

Changes with Repeated Bleaching and Re-irradiation

The symmetry of the EPR spectra already shows that the hydrogen atoms are not trapped at vacant sodium sites or other general positions, but nevertheless they could still be formed from protons in OH groups replacing sodium to a small extent. If atomic hydrogen is destroyed by an irreversible process like formation of molecular hydrogen, we expect a more or less pronounced exhaustion of this hydrogen depending on the relation between the amount of this disorder and the concentration of atomic hydrogen formed with each irradiation. As shown in Table 2, decreasing formation of atomic hydrogen after each bleaching at 160 °C and subsequent X-ray irradiation (Cu K_α, 40 kV, 25 mA)

Number of cycles	I_A/I_B
1	0.96
2	0.62
3	0.52
4	0.45

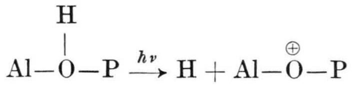
Table 2. Decrease of hydrogen atom center A concentration with repeated bleaching/irradiation cycles.

for 12 hours was indeed observed, but for center A only. The concentrations of the centers B and C remained essentially constant. These variable intensity ratios also facilitated the assignment of the EPR transitions to centers A and B. Three conclusions can be drawn from this result:

1. Destruction of atomic hydrogen is indeed (at least partially) irreversible, and most likely molecular hydrogen is formed.
2. Hydrogen atoms must be trapped close to the sites of their formation. If there are sodium vacancies, they must either be too far away from these sites and/or their trap depth is smaller than for the three C_i sites occupied. Also, the fourth C_i site is not occupied for at least one of the same reasons. Experiments with irradiation and EPR measurements at lower temperatures without warming of the crystal may be suitable to decide between these alternatives.
3. Atomic hydrogen is either formed from additional OH groups or from stoichiometric OH in the neighborhood of additional defects, but not from undisturbed OH groups. Since the amount of replacement of cations by hydrogen is controlled by the accidity of the growth solution, measurements on synthetic compounds grown under controlled conditions may help to remove the remaining uncertainty.

The Role of Atomic Hydrogen in the Formation of Radiation Defects in Brazilianite

Doubtless atomic hydrogen is a primary product of the ionizing radiation, and in view of the other centers formed a process like



$$\mathrm{Al{-}\overset{\overset{\displaystyle H}{|}}{O}{-}P} \xrightarrow{h\nu} \mathrm{H} + \mathrm{Al{-}\overset{\oplus}{O}{-}P} \qquad (1)$$

(where the hole on the right side has also been characterized by EPR [12]) seems very likely. In natural brazilianite the atomic hydrogen is slowly converted into other defects, and evidently it reduces trivalent iron (substituting for aluminium) according to:

$$Fe^{3+} + O^{2-} + H \longrightarrow Fe^{2+} + OH^{-}. \qquad (2)$$

This divalent iron is responsible for the green color of most natural brazilianites. It is thermally unstable above 140 °C and cannot be formed again by ionizing radiation.

The detailed properties of these additional defect centers and their structural implications will be reported in a subsequent publication.

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