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ON SOME PARAMAGNETIC SPECIES INDUCED IN NATURAL
CALCITES BY β AND γ -RAYS IRRADIATIONS

by

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Abstract: We studied the ESR absorption lines of calcite speleothems both as monocrystals and powders, after energetic β -rays or γ -rays irradiation. Both kinds of irradiation produce same lines. Angular variation studies of monocrystals revealed four induced paramagnetic species stable at room temperature. Three of these were attributed to CO_3^{--} group, CO_2^- groups with axial and orthorhombic symmetry and a fourth one could be due to the CO_3^- group. Powder spectra show that these lines, are activated by irradiation in all speleothems we studied and can be present either in natural ESR spectra. Their relationships to the lines usually considered for ESR dating is discussed.

Key-words: ERS dating; Speleothems dating; Calcite monocrystal ESR analysis.

Introduction

In the ESR dating of speleothems (Ikeya 1975), the geological dose of irradiation to which carbonate crystals were exposed is usually evaluated from powdered samples (Ikeya 1978). Several absorption lines responding to radiation doses are generally present. Depending on the spectrometer operating conditions, these lines may appear as simple or composite (Poupeau and Rossi 1984). However, the nature of the absorption lines stable at cave ambient temperature, as underlined by Ikeya (1978) is not yet elucidated.

Marshall and coll. (Marshall et al. 1964, Serway and Marshall 1967, Marshall and McMillan 1968) have shown through ESR and ENDOR analysis that in optical quality single crystals of calcites with no more than a few ppm chemical impurities, irradiation by X-rays, γ -rays and fast neutrons could induce such defects as $\text{CO}_3^{\text{---}}$, CO_3^- and CO_2^- , all stable below 77°K . They also found that the presence of impurities could stabilize these radiation induced defects: It was thus shown that the presence of yttrium stabilizes up to 500°K a carbonate group defect by the constitution of a $\text{CO}_3^{\text{---}} - \text{Y}^{+++}$ ion pair (Marshall et al. 1968) and that a negatively charged impurity, like F^- , may associate to a CO_2^- group to stabilize it to room temperature (Marshall and McMillan 1968). The dating of speleothems by ESR (or Thermoluminescence) involve however radiation-induced defects which must be stable at cave ambient temperatures for times $> 10^6$ yr. Studying by ESR single crystals from the Postjna cave (Yugoslavia), Ikeya suggested that some absorption lines stable up to 600°K could be due to $\text{M}^{+++} - \text{CO}_3^{\text{---}}$ pairs while isotropic defects stable up to 700°K were tentatively attributed to fission-tracks or α -tracks (Ikeya 1978).

In this work, we report ESR analysis in X- and Q-bands of calcites from two brazilian caves, studied as monocrystals or powdered material. Our aims were to try to identify the defects responsible for the dating signal.

Sampling and experimental procedures

The samples selected for single crystal study are two stalagmites from respectively the Santa Barbara (Bahia) and Santana (São Paulo) caves. In hand specimen they appear as well crystalized, the Santana sample being nearly translucent and the Santa Barbara yellowish-opaque. X-ray diffraction characterizes these speleothems as "pure" calcite while Atomic Absorption Analysis reveals some chemical impurities with the presence of 2 to 50ppm Fe group metals. Absence of detectable Si or Al indicate however that no clay or other detrital silicate is present.

Monocrystals of up to 3mm could be easily cleaved out of these samples. They were then cut either parallelly or perpendicularly to the [111] crystallographic direction, the orientation of the sawing plan being checked by X-ray diffraction. Powdered samples from various brazilian and french caves were studied in the 177-250 μm grain size.

The samples were irradiated in air either by a ^{60}Co γ -rays source delivering 12 rads/min or by energetic electrons accelerated in a 2 MeV linear accelerator. Powdered samples were mainly exposed to the ^{60}Co source. All ESR analysis (as well as irradiations) were made at room temperature. Measurements in X-band were performed with a E9 Varian spectrometer and in Q-band with a E12 Varian spectrometer. Resonance cavities were operated in the TE 011 mode and the spectrometer magnetic field was monitored with a Systron-Donner 3193 gaussmeter.

Results and Discussion

Single crystals from the Santa Barbara stalagmite present a natural ESR spectrum with weak lines sensible to radiation doses, while no such lines were present in the Santana cave specimen. When irradiated in the laboratory however, numerous lines stable at room temperature appeared in the g region from 1.9970 to 2.0160. In both samples four paramagnetic species, A, B, C and D (Fig. 1) were recognized in monocrystal studies. Their principal g values, as identified in X-band, are given in table 1. Identification of the paramagnetic defects (table 1, last column) responsible of the presence of these lines was based both on angular variation studies as well as response to microwave power.

The A species is the most sensible to laboratory doses radiation. It presents an axial symmetry perpendiculary to [111] and a 90° symmetry parallelly to it (Fig.2). This symmetry as well as principal g values are same as those of the CO₃⁻⁻⁻ group identified by Serway and Marshall (1967) and thus this species is attributed to that defect.

The B species is characterized by very narrow (= 0.2 gauss) lines. Its spectrum could be completely resolved only for the Santa Barbara calcites, (Fig. 1b) after very high doses of β-irradiations. This species presents a 60° symmetry perpendiculary to [111] and a 90° symmetry parallelly to this direction, which indicates that it is situated in same crystallographic plan as the CO₃⁻⁻⁻ group (Fig.3). It has all characteristics of the orthorhombic CO₂⁻ species described by Marshall and McMillan (1968).

TABLE 1

g factors of paramagnetic species of Santa Barbara and Santana cave speleothems.

Species	Sample	Saturation Power mW	g _{zz}	g _{xx}	g _{yy}	Probable Attribution
A	SB	2	2.0018	2.0034	2.0034	CO ₃ ⁻⁻⁻
	Sa	2	2.0021	2.0035	2.0035	
B	SB	0.5	2.0026	2.0018	1.9972	CO ₂ ⁻ (ortho)
	Sa	0.5	-	-	-	
C	SB	2	2.0028	1.9991	1.9991	CO ₂ ⁻ (axial)
	Sa	2	2.0031	1.9994	1.9994	
D	SB	5	2.0164	2.0142	2.0126	CO ₃ ⁻
	Sa	5	2.0163	2.0143	2.0128	

Additionally, in the spectra taken perpendicularly to [111], one can observe (Fig.1b) a triplet of lines with same intensity and successive width line separation of respectively 1.5 gauss and 1.2 gauss. These separations widths are conservative when observation is made in Q-band (Fig 1c), which indicates the presence of hyperfine interaction with an ion of nuclear spin 1. From the intensity of this triplet, we tentatively attribute it to a nitrogen ion. Species B would therefore appear as a CO₂⁻ complex stabilized by a nitrogen ion in substitution to a CO₃⁻⁻⁻ group. Second order effects affecting the hyperfine line spacing are discussed elsewhere (Rossi et al., in preparation).

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Species C presents an axial symmetry perpendicularly to [111] and a 90° symmetry parallelly to it (Fig.4). It presents all characteristics of the CO_2^- group with an axial symmetry that McMillan and Marshall (1968) attributed to a rotating CO_2^- ion.

Finally, the D species presents an orthorhombic symmetry of 60° perpendicularly to [111] (Fig.5) and 90° parallelly to it (Fig.6). It could therefore correspond to the CO_3^- species of Serway and Marshall (1967). However, contrarily to previous species, the principal g values we found are slightly different of those given by Marshall, of respectively $g_{zz} = 2.0055$, $g_{xx} = 2.0132$ and $g_{yy} = 2.0194$.

Powder spectra of these stalagmites as well as stalagmite YC62 (Caune de l'Arago, France) and of the Matozinho Cave (Minas Gerais) are displayed in Fig.7. These spectra are either natural ESR spectrum (Matozinho), or spectra taken after γ -rays (YC62, Santana) or electrons (Santana, Santa Barbara, YC62) irradiations. In all these spectra, the absorption lines characteristic of A, B, C and D species of table 1 are present.

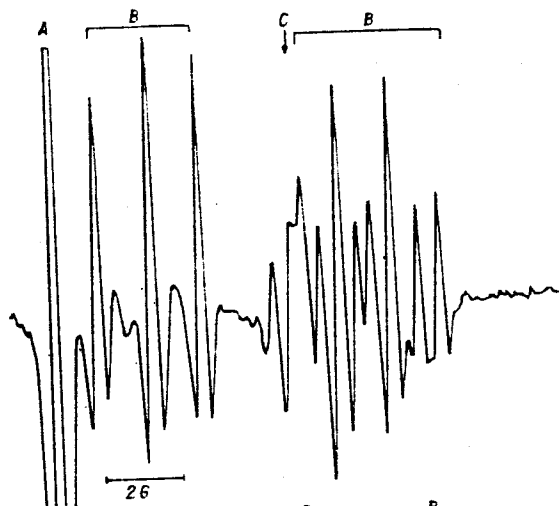
In addition they present two more lines, h_1 and h_3 (see Fig.7) with a $g = 2.0005 \pm 0.0003$, which were not observed in single crystals. The intensity of the h_3 line is significantly smaller in the most heavily irradiated samples (i.e. powders exposed to the electron source). Possibly the even higher radiation doses to which monocrystals were submitted before angular variation studies prevented us to detect this line. The parasite line associated to h_3 has been interpreted as a tribo-effect which can be removed by chemical treatment (Poupeau et al., this meeting). This parasite line saturates at a power of $\approx 5\text{mW}$.

In ESR dating of speleothems, up to three "lines" were frequently considered, dubbed h_1 , h_2 and h_3 by Yokoyama et al. (1981). A in our working conditions, with a Klystron power of 0.2 mW and a 40 gauss scan range, the $h_2 + h_3$ region appears as complex, with some components saturating near to 1 mW. This may have consequence as to its use in geochronology.

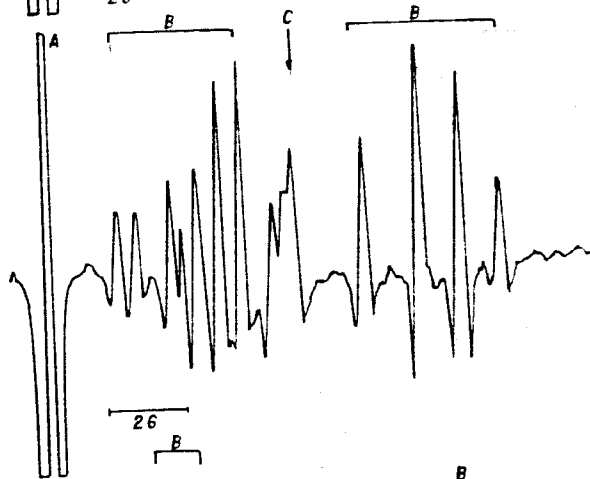
Conclusion

We have identified four paramagnetic species induced by ionizing radiations which are stable at room temperature in stalagmitic calcites. These species are: CO_3^- -group with axial symmetry, CO_2^- groups with axial or orthorhombic symmetry, and a fourth one which has principal g values very nearby to those determined by Serway and Marshall (1967) for the CO_3^- ion. Some of the absorption lines associated to these species contribute to the h_2 absorption line identified by Yokoyama et al. (1981) as part of the dating signal of speleothems. The structural defects associated to the other lines, h_1 and h_3 , of this signal, were not detectable in our monocrystal studies. The relevance of the species observed in this work for ESR dating (thermal stability, saturation doses, etc...) will be considered in a further study.

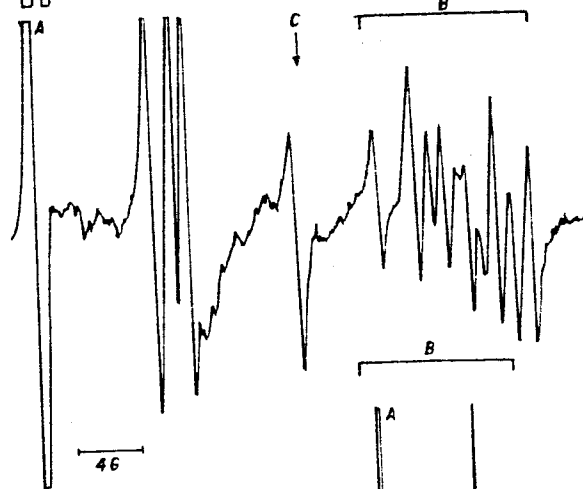
1a. X-band
 $\perp [111], \theta = 0^\circ$
 $\nu = 9,170 \text{ MHz}$



1b. X-band
 $\perp [111], \theta = 60^\circ$
 $\nu = 9,170 \text{ MHz}$



1c. Q-band
 $\perp [111], \theta = 0^\circ$
 $\nu = 35,740 \text{ MHz}$



1d. X-band
 $// [111]$
 $\nu = 9,158 \text{ MHz}$

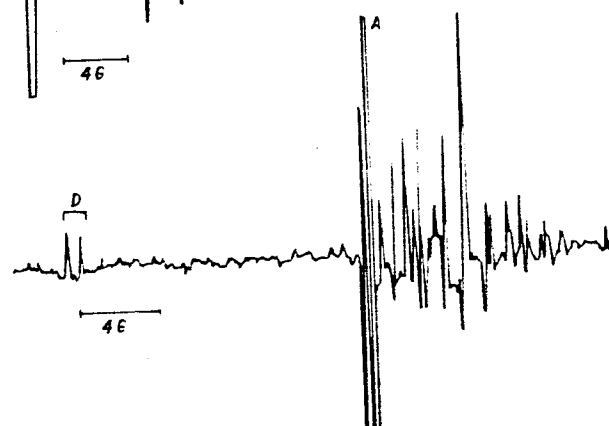


FIG. 1
 ESR spectra of monocrystals
 irradiated with electrons

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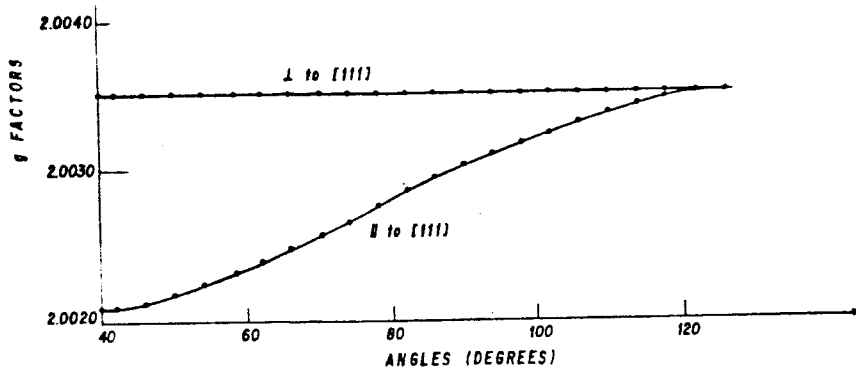


FIG. 2

Angular variation of g factors of species A in a Santana calcite monocrystal.

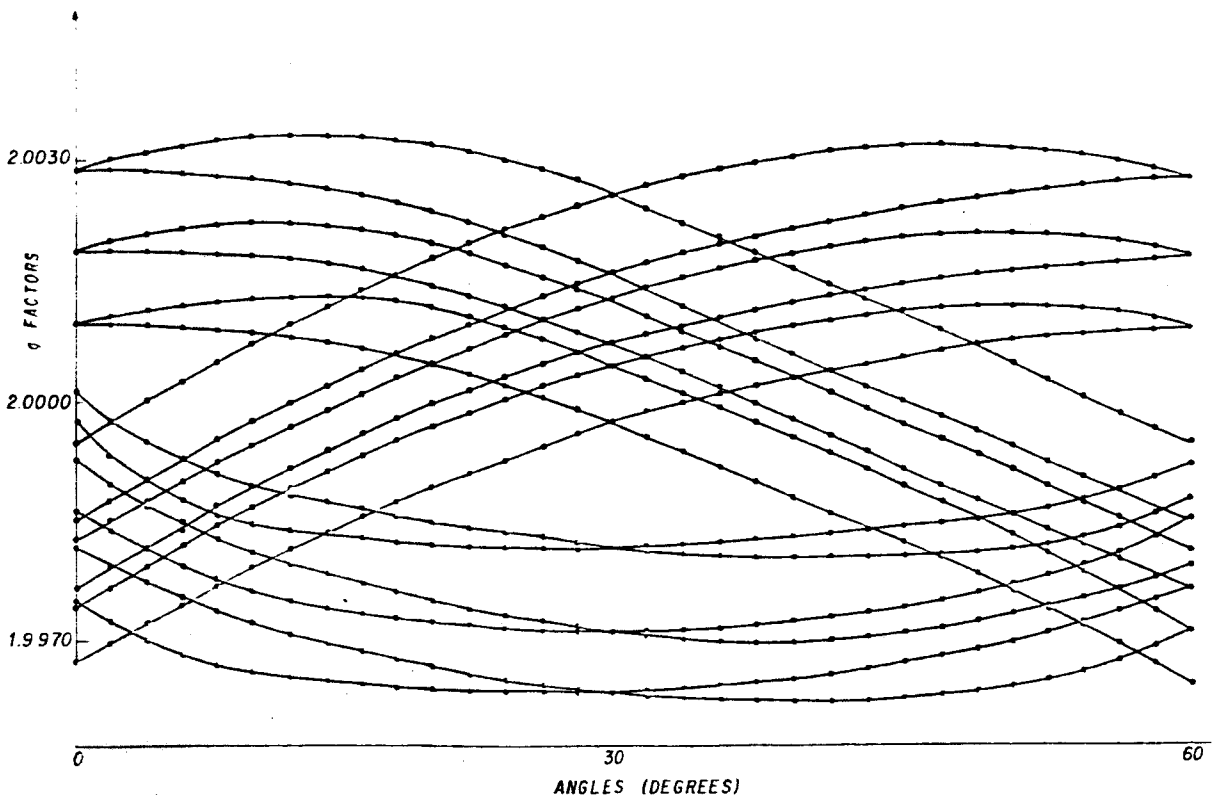


FIG. 3

Angular variation of g factors of species B in a Santa Barbara calcite monocrystal in a plane perpendicular to [111].

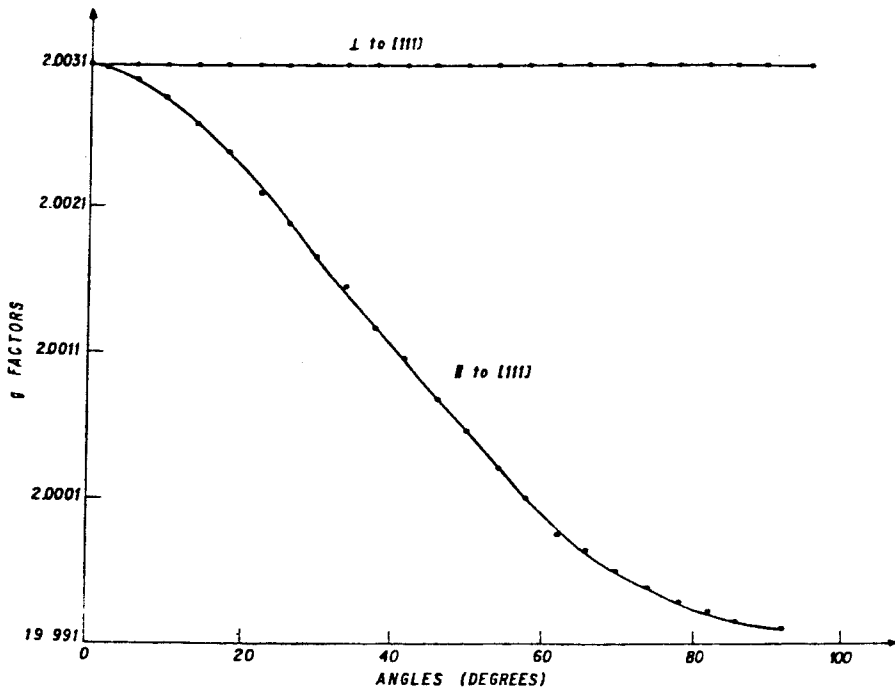


FIG. 4

Angular variation of g factors of species C in a Santana cave calcite monocrystal.

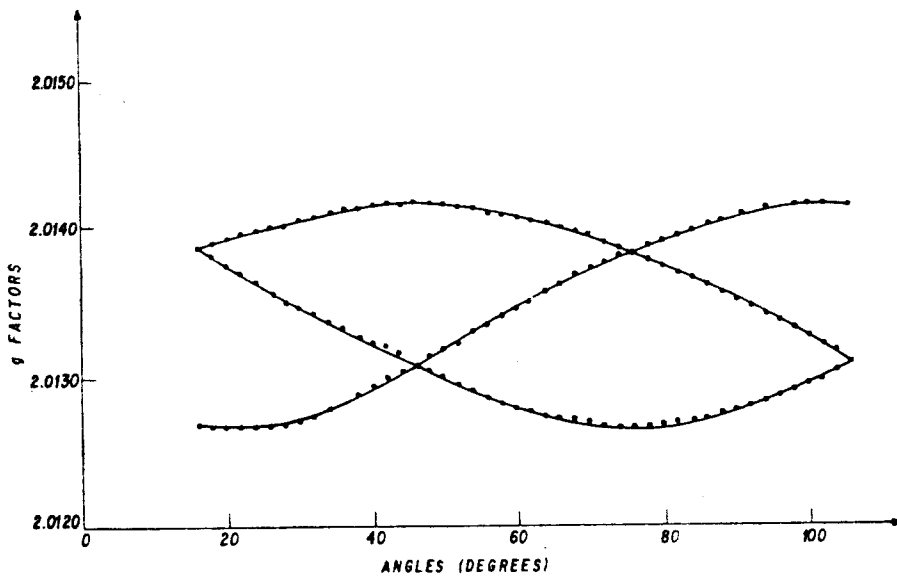


FIG. 5

Angular variation of g factors of species D in a Santa Barbara cave calcite monocrystal perpendicular to [111].

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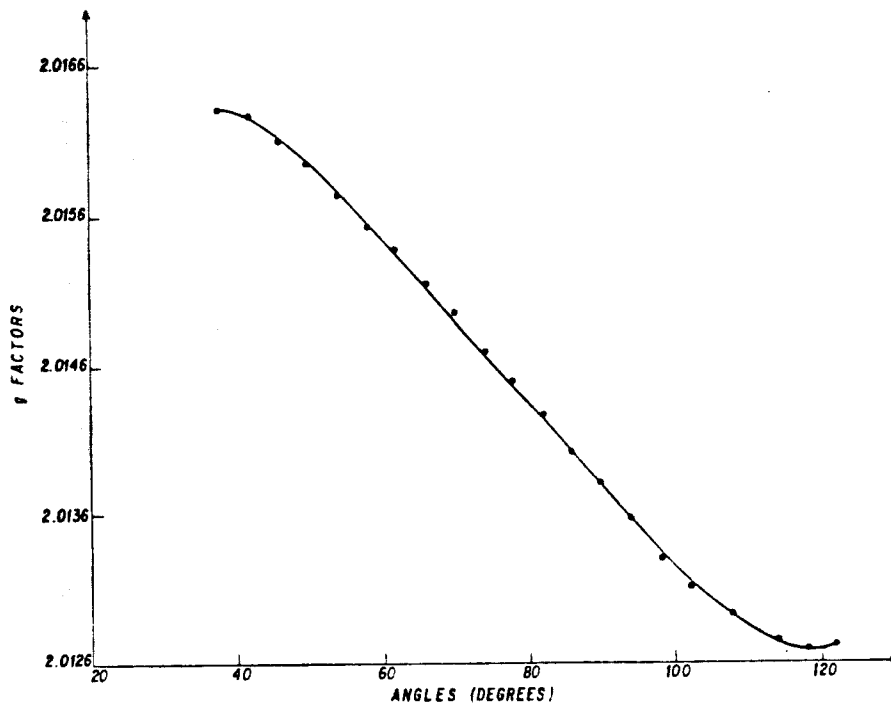
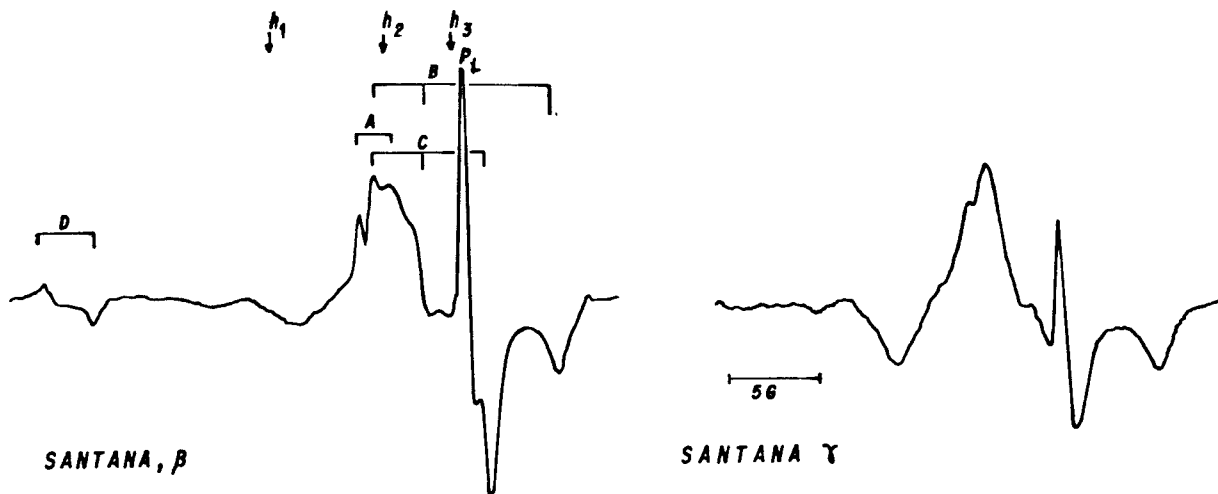


FIG. 6

Angular variation of g factors of species D in a Santa Barbara calcite monocrystal parallel to $[111]$.



3.380 H (GAUSS) 3.400

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