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ELECTRON SPIN RESONANCE (ESR) AND THERMOLUMINESCENCE (TL) STUDIES OF STALAGMITIC FLOORS OF THE CAUNE DE L'ARAGO AT TAUTAVEL (FRANCE)

by

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ABSTRACT

The geological radiation dose to the stalagmites of various stratigraphic levels of the Caune de l'Arago at Tautavel has been measured by Thermoluminescence (TL) and Electron Spin Resonnance (ESR). In all samples the TL natural spectrum exhibit a well developped 280°C peak and a subordinate 350°C peak, while the ESR line spectrum may present the h_1 h_2 and h_3 radiative lines of Yokoyama et al. (1981) or only h_2.

All TL peaks and ESR lines do increase with the laboratory applied radiation (β or γ) doses. The activated h_2 line is visibly unstable in laboratory conditions as well as apparently the h_3 line in one sample. Within the experimental precision, the geological doses determined from the 280°C peak and h_3 line on one hand and the 350°C peak and h_1 line (after thermal treatment of the later, see Yokoyama et al. 1981) on the other hand are identical. When the 280°C natural peak is visibly affected by natural fading as shown by the plateau test, so is h_3, and the geological doses of the 280°C-h_3 peaks are lowered by the same factor as compared to those of the 350°C-h_1 peaks.

Annealing experiments show that the relationships between the TL and ESR peaks may be difficult to analyse in some samples due to the possible occurence of non radiative components in some ESR lines. Such components appear clearly at temperatures above ∿ 180-200°C and might possibly be present below. This may have important implications for the selection of samples to be dated by ESR.

RESUME

Les premières tentatives de datation par thermoluminescence (TL) et Résonnance Paramagnétique Electronique (RPE) du site archéologique de la Caune de l'Arago à Tautavel effectuées dans différents laboratoires ont donné des résultats souvent contradictoires (Colloque International du CNRS à Tautavel, 1981). Les désaccords (jusqu'à un facteur 3) se situent au niveau de l'évaluation de la "dose géologique" d'irradiation enregistrée dans un échantillon. Nous avons donc décidé d'entreprendre une étude systématique par TL et RPE des mêmes échantillons de stalagmite afin d'identifier l'origine de ces divergences, la variété des approches expérimentales et des échantillonnages ne permettant pas pour le moment une comparaison directe entre laboratoires. Nous présentons ici les premiers résultats de cette étude, obtenus sur cinq échantillons déjà datés par certains d'entre nous (Yokoyama et al., 1981, 1982a, 1983) en RPE.

Nos échantillons proviennent donc des mêmes specimen que aux analysés par Yokoyama et al. Toutefois, étant donné l'inhomogeneité de ces stalagmites, la forme des spectres RPE peut présenter quelques différences. Le spectre naturel de RPE mesuré dans divers fragments de nos échantillons montre en effet une certaine variabilité, avec la présence soit des trois raies d'irradiation h_1 h_2 et h_3 (selon la terminologie de Yokoyama et al. 1981) soit celle de la seule h_2. Par contre, le spectre de TL-naturelle présente toujours les deux pics caractéristiques des calcites naturelles à 280°C et 350°C.

Sous l'effet de rayonnements β ou γ, l'ensemble des raies EPR et des pics de TL voient leur intensité augmenter avec des sensibilités spécifiques, la raie h_2 présentant cependant une instabilité déjà très visible dans les conditions du laboratoire. Les doses d'irradiation géologique mesurées à partir de la croissance de h_3 (RPE) et du pic de 280°C (TL) sont identiques, à notre niveau de précision expérimentale, de même que celles obtenues à partir de h_1 (après traitement thermique, voir Yokoyama et al., 1981) et du pic de 350°C. Quand le pic de 280°C est affecté d'un "fading" naturel, il en est de même du pic h_3 et la dose calculée à partir de h_3 ou de ce pic sont minorées du même facteur par rapport à celle déduite de h_1 ou du pic de 350°C.

Des expériences de recuit thermique en régime isochrone et isotherme montrent que l'analyse des relations entre raies EPR et pics de TL peut être gênée par la présence de lignes parasites RPE d'origine non-radiative. Ces derniers composants apparaissent nettement à des températures supérieures a 180°C-200°C et pourraient exister à de plus basses températures. Ceci peut avoir d'importantes implications our le choix des échantillons en ce qui concerne les datations par RPE.

1. INTRODUCTION

The Tautavel Man, represented at the Caune de l'Arago by some 60 tooth and bone remains, including a nearly complete cranium, appears a key fossil in the european phyllum of Homo Erectus, and as such deserves a precise dating (M.A. de Lumley, 1981). Under the impulsion of Prof. H. de Lumley, numerous efforts were undertaken in this direction since several years and as a consequence nearly 20 groups presented their results at the 1981 Tautavel Colloquium. This cooperative project produced a wealth of data but also some embarassment as regards to the wide discrepancies between ages produced in different laboratories using same or different dating techniques. Part of these discrepancies are a consequence of the old putative age of this site, of $\sim$ 500 000 yr (as suggested by the fauna associated with the humain remains), for which there does not exist yet well established dating methods. Another reason, specific to the site itself, is that running water action was eased within this limestone cave by a recent (10^5 yr ago?) fall of the central part of the roof which gave to surface waters from the overlying karstic plateau a direct access to the cave (de Lumley et al. 1981).

Numerical datings at the Caune de l'Arago were led on fossil bones and stalagmites. Evidences were brought from different directions that most bones had behaved as open systems and could not be considered as reliable chronometers (Tautavel Colloquium, 1981). Clues to age divergences in limestone floors were suggested by Yokoyama et al. (1982c) who showed

(i) that recent uranium deposition would affect more U-series desequilibrium than Electron Spin Resonnance (ESR) or Thermoluminescence (TL) ages, (ii) that the degree of rejuvenation of U-series ages were clearly correlated with the situation of sampling in the Tautavel cave as regards to water circulation. Still, strong divergences (up to a factor 3) do exist in the evaluation of the ages of different stalagmitic floors between different laboratories applying TL or ESR geochronology. The major disagreements apparently come from the way the geological doses to the samples are estimated. However, comparing the data obtained in various places is difficult because of a lack of uniformity in sample preparation as well as the diversity of the samples themselves. For these reasons, we decided to re-investigate by TL and ESR the five stalagmitic floor samples already dated by ESR by Yokoyama et al. (1981, 1982a). We present below the first results of this program. They have been obtained in the TL and ESR laboratories of the Centro Brasileiro de Pesquisas Físicas.

2. SAMPLE DESCRIPTION

The five samples studied come respectively, following the terminology of the Lumley et al. (1981), from the upper stalagmitic floor (YC26), the stalagmitic floor of stratigraphic ensemble IV (YC5, YC7, YC18) and the lower stalagmitic floor (YC62). All have been chipped from the hand specimen already dated by Yokoyama et al. (1982).

Sample YC26 is a layered stalagmitic floor. Over its 20mm thickness, four main layers numbered I to IV, from top to bottom, are visible to the naked eye (Fig. 1). Levels I, II and IV are yellow (I,IV) to nearly white (II) while level III is a dark unit. Five samples were taken for TL-ESR studies. From our past as well as others (see f.i. Ikeya, 1978) experience, it appeared that dark layers in stalagmitic material are unconvenient for ESR dating, due to clay contamination. Here too the layer III sample revealed unusable.

In sample YC5 and YC7, no obvious layering is recognisable and therefore no special caution was taken to extract materials. Sample YC62 shows a series of clear layers from wich samples were taken for analysis.

Sample cutting from original fragments was made using diamond dental tools. For all samples a slab was kept for a further microanalysis of the uranium distribution by the fission-track method. Where layering was apparent, the slab was cut perpendicular to it.

3. THERMOLUMINESCENCE

3.1 Analytical procedures

The samples, after gentle crushing by percussion in an agathe mortar and sieving, were studied as powders in the 74-120μm range. When no other additional treatment as dilute acetic acid (1% solution at 25°C for 1 to 2 minutes) washing followed by distilled water rincing was applied, triboluminescence was found to affect strongly even the 280°C nominal peak (Fig. 2). This tribo-TL was effectively eliminated by a further exposure of the powder to a saturated boric acid solution for two days at room temperature, a procedure shown by Valladas et al. (1982) on a sub-sample of YC62 not to affect the measurement of the geological dose.

The TL was observed in the blue region of the optical spectrum (350-500 nm) with a heating rate of 10°C/sec, from room temperature to 500°C. The "geological dose" was determined following the incremental dose method (Aitken, 1974). β-irradiations were performed with a ^{90}Sr source of 50 mCie, each TL reading being made on an 3 mg powder aliquote. For each β-dose, the TL was measured on at least 5 and up to more than 10 aliquotes. Depending on the sample, the reproductibility (1 standard error) of TL measurement was found to vary from ± 3% (sample YC18) to ± 8% (samples YC5). For each sample, enough powder was prepared to allow several determinations of the geological dose. Repeats of the geological dose measurements gave results in agreement to within ± 5% even when TL readings were separated in time by up to several months.

3.2 Results

One powder was prepared for each sample, from an area where clear calcite was present, in order to minimize clay contamination. The TLN exhibits the classical "280°C" and "350°C" peaks of the natural calcites, which are recorded in our measuring conditions at 300°C and 370°C. A third peak is induced by β-irradiations at 130°C (Fig. 3). Following previous authors (Wintle, 1978; Valladas et al., 1982), we first considered for the determination of the geological dose, the nominal 280°C peak. To a first approximation, both the first and second glow curves of all samples are linear up to laboratory doses of 10 to 20 krads (Figs. 4 to 6). The β-equivalent doses do vary from 4.4 krads for sample YC26 to 11.4 krads for YC62 (Table 1). The slope of the second glow growth curve is about the same or lower by up to 40% than that of the first glow curve. Supralinearity affects measurably only samples YC7 and YC18.

For both the 280°C and 350°C peaks, the TL was measured at the maximum peak height. Due to the poorer reproductibility of the 350°C peak shape, the precision of the total dose tends to be lower than for the 350°C peak.

The TL growth curve of the 350°C peak has been studied to date only for YC7 and YC18. In the former sample, the TLN + dose growth curve is linear up to laboratory doses of nearly 30 krads. The second glow growth curve presents a higher sensitivity to dose than the first glow curve, and is not affected by supralinearity (Fig. 5). The geological dose to the 350°C curve as deduced from the first glow curve is of the order of 30 krads. In YC18, the response to γ-dose of the second peak is sensibly different, as it was found that the TLN is already very near to saturation. Still, its second glow curve growths linearly, without supralinearity, up to laboratory β-doses of 14 krads (Fig. 6).

Assuming no major change in sensitivity and saturation level occured after the first heating of YC18, one can deduce from a linear extrapolation of the TLA growth curve of this sample that it was exposed to a geological dose of the order of 15 krads. In both YC7 and YC18 the sensitivity of the 350°C peak was found to be considerably lower than those of the 280°C peak, and its geological dose significantly higher (by about a factor of 3). Other authors also used the 280°C and 350°C TL peaks as well as ESR to measure the geological doses to stalagmitic floors for various levels of the Caune de l'Arago. Their results are reported along with ours in Table 2. The total doses we find for the 280°C peak of our samples are comparable with those found by others (Valladas and Yokoyama, see refs. 2 and 4 of Table 2) for the same hand-specimen samples, either using this TL peak or the h_3 ESR peak (see also Tautavel Colloquium, 1981). Samples YC7, YC18 and YC62 have been studied both by TL and ESR. It is interesting to note that the ratio of the geological doses of the 280°C to 350°C TL peaks and the h_3 to h_1 ESR lines present similar values in the range from 0.30 to 0.39, suggesting (i) some sort of relationship between the 280°C TL peak and the h_3 line on one hand and the 350°C peak and h_1 on the other hand. Our own results (see below) suggest this relationship might be far from simple, (ii) that the 280°C peak (and h_3 line) are affected by some fading , which is confirmed by the shape of the plateau-test curve in f.i. YC7 (Fig. 7).

The results of Debenham in Table 2 are at variance with the other data for the lower stalagmitic floor, in terms of the ratio of equivalent-doses. In effect, this author finds values of 0.82 to 0.92 for the 280°C/350°C geological doses ratios. Given the analytical precision of these measurements, this means that the degree of non-thermal fading affecting the 280°C peak of Debenham samples might vary form essentially zero to at most 30%, against ∿ 70% for ours.

Debenham considers, on the basis of his measurement of the mean life of the 280°C, that the "true" geological dose would be obtained by this same peak. In fact, there is not yet any consensus about the lifetime of this peak. In an earlier work, Wintle had derived from annealing experiments on several calcites, a mean life at 15°C of the 280°C peak of of 3×10^7 yr, a value much higher than found by Yokoyama et al. (1982b), of 2×10^5 yr, from YC62 data.
The value computed by Debenham (1983) of 10^6 yr, is in fact, due to its limited precision, compatible both with those of Wintle and Yokoyama et al. On our own, we prefer to consider on the basis of plateau-test (see also Valladas data and our results in Table 2), as Yokoyama et al. (1982b) that for some yet unknown reason, the 280°C peak may behave differently in different samples. Evidences for the occurence of natural fading of the 280°C peak in natural calcites were in reality already discovered a few years ago. In the Proceedings of an earlier Specialist Seminar on TL dating, Bangert and Henning (1979) had pointed out that in some stalagmites their 270°C TL peak presented some fading, and they recommended the use of the 330°C peak for TL dating, on the basis of the plateau-test (their Fig. 2).

To conclude, our present results suggest that actually the behaviour of the 280°C as regard to equivalent-doses determination for "old" (i.e. $\gtrsim 5\times10^4$yr) samples is yet unpredictable and that some of the contradictions in the comparison of TL and ESR datings of the Caune de l'Arago stratigraphy may have come from the non-recognition of the 280°C peak variability. Further work is therefore needed to better characterize the properties of this peak and use it in TL dating.

4. ELECTRON SPIN RESONNANCE

4.1 Experimental procedures

To date, we started ESR studies on YC26, YC18 and YC62. Powders were prepared in same way as for TL studies, except for acid treatment. For YC26, one sample from each of the layers I to IV (Fig. 1) were measured, as well as one powder labeled YC26 ATL, already studied by TL. The ATL sample comes from a position roughly equivalent to ESR sample II (Fig. 1).

Our ESR spectrometer, a Varian E9 tuned at a microwave frequency of 9 GHz (63 mW power) and a field intensity of 3400 Gauss, was equipped with a rectangular resonance cavity operating on a TE 102 mode. Removable devices to this cavity were designed to ensure a good reproducibility of the sample positionning. All powders were measured from weighed fractions of 50 mg introduced within silica glass tubes. γ-irradiations were performed with a ^{60}Co source from the Radioprotection and Dosimetry Institute of the brazilian National Commission for Nuclear Energy in Rio de Janeiro, a primary laboratory for radiation dosimetry in Southern America. The source delivers 17 rads/mn in our samples. All irradiations were monitored by a Fricke solution with a precision of 1%. As Yokoyama et al. (1981a), we considered the dose to the sample as being the same as to the Fricke solution. It has been observed that no more than 24h at room temperature were sufficient to stabilize the radiation-induced ESR signal to the samples, and that thereafter this signal kept constant - within 5% - at least up to 4 months (see below).

As generally not much sample powder was available, we adopted the following procedure for the geological dose determination by the additive dose method:

1 - weight 50 mg of powder into a silica glass tube of 25 cm in lenght. Read its natural ESR.

2 - The tube being sealed at its two ends, take it upside down for γ-irradiation (Fig. 8).

3 - 24 hours at least after irradiation set the tube in its initial position for ESR spectrum recording.

This procedure avoids any γ-induced signal to the quartz glass to interfere with the sample signal. In effect, in our irradiation geometry the part of the tube (B in fig. 8) used for ESR measurements is never exposed to the ^{60}Co rays. Both irradiations and ESR spectrum recordings are made at room temperature. However, the use of a small sample size has some consequences as regards to the ESR signal. In effect, whereas the h_3 line intensity growths regularly with the microwave power from 4 mW to at least 65 mW, the h_1 and h_2 lines start to saturate between 15 and 20 mW. As a consequence, only the results on h_3

may be considered for quantitative (i.e. geological doses) anal ysis. For annealing experiments, measurements were made both at 63 mW and 10 mW without essential difference in the ESR spectra.

The ESR line spectrum were measured as peak heights, not surfaces, due to the difficulties to define and integrate the later (Yokoyama et al. 1981). For each ESR reading, the radiation induced peaks h_1 h_2 and h_3 (Yokoyama et al. 1981) as well as the nearest Mn^{2+} lines were computed.

The Mn^{2+} lines do show some systematic variations with the laboratory doses, up to 20% for 40 krads, and therefore could not be used for normalisation purposes. The spectrometer was constantly monitored with a 50 mg YC62 unirradiated powder used as a standard.

Each sample measurement was doubled by a YC62 standard measurement. The maximum variations of the spectrometer response to this standard for a given set of tuning parameters, over a period of 4 months if of ± 10% with a standard deviation (one sigma) of ± 5%. Within any single day, the variation is within ± 2%.

4.2 Response to γ-doses

The effect of additive laboratory γ-doses has been studied on 3 samples of YC26, from layers I, II and IV, prepared without chemical treatment, and YC26 ATL, the power already measured by TL. The natural ESR spectrum of the 3 untreated samples do present only the h_2 peak of Yokoyama et al. (1981, 1982a), the h_1 and h_3 peaks appearing progressively only upon irradiation. In YC26 ATL, the three h lines are present in the natural ESR spectrum (Fig. 9). The g values are the same within the precision of our measurements, for all samples, at $g_1 = 2.0056 \pm 0.0003$, $g_2 = 2.0025 \pm 0.0003$ and $g_3 = 2.0006 \pm 0.0003$ (one standard deviation around the mean value). These values are not very different from those measured by Yokoyama et al. (1981, 1982a). Note that when our gaussmeter is kept along the resonnance cavity while taking ESR spectra, identical values as Yokoyama et al. are found. The presence of the gaussmeter introduces some modulation in the magnetic field, which results in a loss of resolution in the sample peaks. It was therefore removed for ESR spectra measurements. According to the samples, from 3 to 4 γ-doses were successively applied up to a total of 30 krads (sample ATL) to 64 krads (samples I, II and IV). No thermal treatment was given to the samples after γ-irradiation, the time between each ^{60}Co exposure varying between 1 to more than 5 months. We observed that the three h lines are sensitive to γ-irradiation and increase with the γ-dose. Stabilization of the signal for h_1 and h_3 takes about 24 h. Afterwards, only h_2 continues to decrease significantly, losing from $\sim$ 25% to $\sim$ 80% of its height within the next 100 days. The h_1 and (generally) h_3 peaks stand constant within the precision of our measurements. In sample YC26 II, the h_3 peak can loose up to more than 10% during the same period.

Due to the instability of the h_2 peak excited by the ^{60}Co irradiation and saturation (see 4.2) no "geological dose" could be computed from our data for samples YC26 I, II and IV, where h_2 is the only line of the natural spectrum. In 26 ATL, were the h_1 and h_3 peaks are present in the natural ESR and grow linearly with dose (Fig. 13), a backward extrapolation for h_3 gives a "geological dose" of 4.2 krads. This is of the same order as found for the 280°C TL peak (Table 1). As usual, the doses of the h_3 or 280°C peaks are significantly lower than that of the h_1 line thermal treatment, as for the same sample, Yokoyama et al. (1982a) found a "geological dose" to the latter of 6 krads.

As we do not have TL data about the 350°C peak for this sample (Table 1) it is not known wether the highest dose of h_1 would correspond to this peak or to the presence of a non-radiative component in h_1 (see below and Skinner, 1983). There are at least suggestions from the shape of the plateau-test up to 350°C that in effect the 280°C peak might be affected by some fading and therefore that the ∿ 4 krads dose of the h_3 and 280°C peaks might represent only a lower estimate of the geological dose. The matter however would require additionnal studies on new samples.

4.3 Relationship between the ESR and TL peaks

As underlined by Skinner (1983), the relationship between ESR and TL peaks is not necessarily a trivial one, and there is yet no consensus on the subject. On the basis of annealing experiments, the 280°C TL peak has been claimed by Valladas et al. (1982) to correspond to an ESR peak with g = 2.003, thus the h_2 + h_3 peak, while Yokoyama et al. (1982b) admit the same TL peak would correspond to the h_3 ESR line.

Debenham affirms that there is no justification to identify h_3 with the 280°C TL peak. Similarly, while Valladas et al. and Yokoyama et al. suggest that the ESR transition occuring at g = 2.007, i.e. the h_1 line might be associated to the 360°C TL peak, the results of Skinner show that at least a fraction of the h_1 trapped electrons are not related to those giving this TL peak.

Unfortunately, due to a shortage of YC26 sample, we could not perform annealing experiments in order to test the claim of Valladas et al. about the identification of $h_2 + h_3$ to 280°C TL peak.

We could however perform this kind of experiment on YC18, which exhibits in its natural spectrum 3 well developped h peaks. We successively annealed in our TL oven a series of aliquotes in the same heating conditions as for TL analysis, up to temperatures of 325°C (to eliminate the nominal 280°C peak) and 418°C (to eliminate the 350°C peak). The powders were then analysed in the ESR spectrometer. The results, displayed in Fig. 10, show the relative behaviour of the h and neighbouring Mn lines. All spectra were measured in same conditions and their peak intensities monitored by a standard. While the Mn line height kept constant (within 5%) even after a heating to more than 400°C, the h lines showed remarkable behaviours, h_3 having yet been totally annealed at 325°C, where h_1 had grown to five times its natural height before regressing considerably, but still above its natural level, at 418°C. More intriguing perhaps was the evolution of h_2, whose behaviour after γ-irradiation suggests this line is the most thermally unstable (see above and Yokoyama et al., 1982b): in the experimental results reported in Fig. 10, h_2 is the only peak to grow continuously with temperature.

Strong h_2 line in natural YC18 sample seems due to a carbon radical line which is situated near the real h_2 line due to radiation effect (Yokoyama et al. 1983). YC18 is an altered sample which shows a young U-Th age in contradiction with its stratigraphical position (Yokoyama and Shen 1983).

The enormous increase of this peak above 400°C corresponds to the observation made by Apers et al. (1981) who noted, starting at about 350°C, the emergence of a new line in the spectrum of their "Tautavel 2" sample, at a g value (2.0029) very near to the g value of the h_2 line. They suggested that this new line resulted from the pyrolysis of organic matters, because this phenomenon does not occur in the pure synthesized calcite.

The 4 samples studied in ESR: YC18, YC26, YC26 ATL and YC62, were re-examined with a different set of spectrometer parameters. With this new settings, two lines, h_2 and h_2^*, instead of one could be resolved in the vicinity of g = 2.0030. In sample YC62, the h_2 line, at a g value of 2.0035, behaves as the h_2 line of Yokoyama et al., i.e. disappears with moderate thermal treatment. In the other 3 samples, the natural spectrum presents a h_2^* line at a g value of 2.0025. In these samples, this line increases with thermal treatment and it is this h_2^* line which is responsible of the behaviour described in this paper. Investigations are in progress to study the differential behaviour of these h_2 and h_2^* as regards to γ-irradiation and thermal stability.

In this experiment, the behaviour of h_3 is not in contradiction with its belonging to the 280°C peak.

It has been suggested that the h_1 line is populated from electrons redistributed from the h_2 and h_3 lines (Yokoyama et al., 1981, 1982a). Skinner (1983) and Valladas et al. (1983) supported this suggestion. The large increase (by a factor of 5) noted in the height (and surface) of h_1 from the ambiant temperature to 325°C suggests that, in this sample, the transfer of the electrons from the h_3 trap to the h_1 trap occured with a very good efficiency. This good transfer efficiency is also observed by TL: the TL peak height ratio 350°C/280°C for YC18 is 0.63 which is twice of the ratio for other samples (0.29 for YC62 and 0.33 for YC7). This fact is consistent with the identification of the h_1 line to 350°TL peak.

The persistence of the h_1 line at more than 400°C, at which temperature one would expect the disparition of 350°C TL peak, is explained by the evidently complex nature of the "350°C" TL peak, whose shape presents a long tail up to 500°C, where it becomes masked by the black-body curve. Again the behaviours of h_1 line in this experiment are consistent with its belonging to the 350°C TL peak.

In order to analyze with more details the phenomenon, we proceeded to a series of isochronal experiments between the ambiant temperature and 420°C for YC18 and YC62. In this experiment, each led on a 50 mg powder samples, the <u>same</u> powder was stepwise heated in its silica glass tube for 30 minutes to increasing temperatures, the ESR spectrum being measured between each annealing step.

The results are displayed in Figs. 11 and 12. The 2 samples exhibit a similar behaviour.

- the h_3 peak starts to decay at 180°C and is totally anneealed at 240°C (YC62) to 260°C (YC18)
- the h_2 peak keeps constant up to 200°C in YC18 and 350°C in YC62 before increasing slowly at first for YC18 and very rapidly for both samples above 400°C
- the h_1 peak stands nearly constant up to 180°C in YC18, while increasing of some 50% in the same temperature range for YC62, before enhancing considerably up to 250°C and decay to a fraction of its natural value at 420°C.
- the h_2 above 400°C in both samples, a non-radiative component superposes on the radiation-induced lines. The isochronal annealing experiments thus confirm the data of Fig. 10 and suggest that if, for ESR dating, any thermal treatment has to be applied to natural calcites (see below), it has certainly not to exceed the critical value of ∿190°C.

4.4 Isothermal experiments and ESR dating

In an earlier step of this work, Yokoyama et al. (1981) precisely proposed for ESR dating of calcites a methodology involving a thermal treatment of the samples previous to ESR espectrum measurement. Based on the unstability of h_3 and especially h_2 in γ-irradiated samples and their experimentally verified quantitative redistribution to h_1 by thermal treatment, these authors proposed, to date the stalagmitic floors of the Caune de l'Arago, an original methodology where, previous to any ESR measurement of either the natural or natural + dose spectrum, the samples are heated during 24h at a moderate temperature of 170°C to 190°C (Yokoyama et al. 1981, 1982a, 1983). This procedure, tested on YC62, is supposed to redistribute trapped electrons from h_2 and h_3 within the h_1 peak, all these electrons being assumed to be of a radiative origin.

In order to check the generality of this behaviour, we completed our study of YC18 by treating isothermally this sample at five different temperatures: 80°C, 135°C, 185°C, 200°C and 260°C for times up to 24h. In addition, one powder of YC62 was measured in similar conditions at 185°C, 200°C and 260°C. Only the redistribution of the natural ESR spectrum were studied to date. The experiments were led as follows: aliquotes of the powdered materials were weighed to 50 mg in silica glass tubes and their natural ESR spectrum taken for further normalisation. Each tube was then heated only once for a time between 1 and 24h. Thus annealing curves as those reported in Fig. 14 have been built from as many aliquotes as point measurements, i.e. 19 different tubes in the YC18 200°C isothermal curves. The ESR measurements were taken at a Klystron power of 10 mW and 63 mW, with similar results.

Our YC18 sample reacted almost identically with the YC62 studied by the Gif group for the h_1 and h_3 lines. The difference between YC18 and YC62 is in their h_2 line: this line in natural (and old) samples is principally due to the carbon radical of non radiation origin and hence its intensity widely varies from sample to sample.

Progressive isothermal heating of YC18 up to a total of 24h at 80°C or 135°C did not change the intensity of h_1 h_2 and h_3. At 185°C and 200°C, all peaks are affected, although unequally. Typically (see Fig. 14 for 200°C), h_3 disappears first while h_1 increases and reaches a constant value within the first two hours of heating, while h_2 remains about constant, however after a slight initial increase at 200°C. At 260°C, the temperature is high enough to cause the disappearance of h_3 in less than 15' and affect progressively the intensity of h_1 after an initial increase. Again, h_2 does not seem to be affected and keeps constant up to 3h heating, the longest annealing time at this temperature. This overall behaviour of YC18 seems to be consistant with those we obtained in previous experiments (Fig. 10 and 11)

At temperatures > 135°C, the sum of peak height h_1 + h_3 is not constant, but this is normal because of the difference of line width between h_1 and h_3.

As noted by Yokoyama et al. (1983), there is some danger to work on peak height rather than area. We however continued to use the former due to the wide errors which would be introduced in the double integration necessary to get the absorption signal area.

Our YC62 sample, for which only preliminary data are at hand, exhibit still other responses to isothermal heating. At temperatures of 185 and 200°C ($h_1 + h_3$) keeps constant at first, then decreases. At 260°C h_3 disappears here also within less than 15' allowing h_2 - formerly a shoulder of h_3 - to appear and stay constant as well as h_1 up to 13h heating. This

h_2 may also be due to carbon radical.

5. DISCUSSION AND SUMMARY

The aim of this work was to revisit the relationships between the TL and ESR signals in calcitic materials of the Caune de l'Arago cave as an attempt to decipher the nature of the contradictory dating informations derived from this signals by various laboratories (see Tautavel Colloquium, 1981). This would have involved TL and ESR study of the same materials. Unfortunately, due to various reasons including the ESR or TL behaviour of some of our samples, this goal could not be fulfilled in this first step of our work. Nevertheless, the following results were reached:

1. The wide range of experimentally derived values for the mean life of the 280°C at an ambiant temperature of 15°C, from 10^5 yr to 3×10^7 yr, as found by different authors (Wintle, 1978; Yokoyama et al., 1981, 1982b; Debenham, 1983) suggest that in old calcites it might be possible to find evidences for fading of this peak. We, as well as others (Valladas, in Yokoyama, 1982b) found that in some stalagmite of the intermediate and lower stalagmitic floors at Tautavel the 280°C TL peak could be affected by up to 70% fading, while in others this peak was only marginally affected (Debenham, 1983). In other caves, Bangert and Hennig also found evidences for anomalous fading of the 280°C peak. The behaviour of the natural 280°C peak therefore presents same variations

as might be expected from the range of its computed mean life time. However, the parameter (s) that controls the life time of the 280°C peak (probably a composite one, see below) are yet to discover.

2. For those samples where geological dose determination were made both by TL and EPR, there is in general a remarkable agreement between both methods (see Table 2). The doses derived from the 280°C TL and h_3 ESR line on one hand and the 350°C peak and h_1 (when h_2 and h_3 are thermally redistributed into h_1 as proposed by Yokoyama et al., 1981, 1982a) on the other hand, do agree generally within the limits of error. Thus the only sample in our work where these measurements could be done, YC26 ATL, provide for the 280°C peak and the h_3 line geological doses of respectively 4.4 krads and 4.2 krads. Where the natural 280°C peak is affected by fading, the dose ratio of the h_3 to h_1, instead of equal to 1, is lowered by the same factor as the 280°C/350°C dose ratio. When dating of the same samples by other methods are possible, i.e. by the desequilibrium of the uraniun series, the best agreement is realised (when 280°C/h_3 dose ratios are lower than 350°C/h_1 ratios) with the ages derived from h_1 peak (see Yokoyama et al., 1982b) accrediting the idea that the 280°C or h_3 peaks are "good" dating parameters only when unaffected by natural fading (for an opposite view, see Debenham, 1983). The overall similar behaviour for the determination of the geological doses of the 280°C-h_3 and 350°C-h_1 signals argue in favor of some relationship between the members of these couples.

3. The h_3 peak in the samples we studied (see also Yokoyama et al. 1982b) seems to react to thermal annealing as the 280°C peak.
4. The h_2 peak present in the natural spectrum of the YC18 and YC62 samples we analysed present quite anomalous behaviours. This peak in natural (and old) samples is principally due to the carbon radical of non radiation origin, which explains this anomalous behaviours.
5. The response to the dose of h_1 is not trivial. In the samples studied by Yokoyama et al. 1981, 1982a, h_1 did not respond to the dose. It was then guessed by these authors that only h_2 and h_3 could be populated by the free electrons liberated by ionising radiation, the apparition of the h_1 transition being later the product of h_2 and h_3 electron redistribution into a deeper trap over time at ambiant temperature.

   The behaviour of h_1 in isochronal annealing of the natural ESR exhibits a very strong increase from 150°C to 250°C which decays to a residual value at temperatures in excess of 400°C, in YC18 and YC62 (similar observations were made by Apers et al., 1981, in their "Tautavel 2" sample). The persistence of the h_1 line at more than 400°C, has its correspondence in TL: the evidently complex nature of the "350°C" TL peak which might extend to more than 500°C.
6. Both in our and Apers et al. isochronal treatment of Tautavel samples, the apparition of non-radiation-induced peaks and the complexity of the h_1-350°C peak at a high temperature fixe an upper limit to any thermal treatment for the

redistribution of h_2 and h_3 into h_1, for ESR dating, In effect the Gif group used prolonged annealing times at temperatures between 170°C and 190°C (Yokoyama et al., 1981, 1982a).

As preliminary as they are, our results, as well as those obtained in companion studies by Yokoyama et al. (1982b; and in preparation) suggest some rationality in the comparison of TL ans ESR estimates of geological doses.

Particularly, they show how wide can be the sample to sample variations in TL and ESR responses of stalagmitic materials of the same limestone cave, and the danger to generalize data gathered from a few samples. The relationship between the TL and ESR peaks are evidently complex ones, and further work ahead is needed to fully understand their nature.

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TABLE 1

TL GEOLOGICAL DOSES OF STALAGMITIC FLOORS FROM THE CAUNE DE L'ARAGO

	280C PEAK			350C PEAK		
	β-equivalent dose krads	supra-linearity krads	slope TLN / slope TLA +	β-equivalent dose krads	supra-linearity krads	slope TLN / Slope TLA
YC 26-ATL	4.4 ± 0.3	negligible	1.38			
YC 5	5.9 ± 0.25	0.2 ± 0.1	1.18			
YC 7	10.6 ± 0.3	3.8 ± 0.4	1.17	30.7 ± 2.0	3.7	0.84
YC 18	6.1 ± 0.4	2.0 ± 0.3	1.23	(15) §	no.S.1	
YC 62	11.4 ± 0.2	negligible	1.02			

+ Ratio of the slopes of first glow growth to second glow growth curves.

§ See text

TABLE 2

COMPARISON OF THE GEOLOGICAL DOSES MEASURED IN VARIOUS TL AND ESR PEAKS FOR STALAGMITES OF THE CAUNE DE L'ARAGO

SAMPLE	TL: 280-ED+ krads	TL: $\frac{280C\text{-ED}}{350C\text{-ED}}$	TL: Ref	ESR: h_3-ED	ESR: $\frac{h_3\text{-ED}}{h_1\text{-ED}}$	ESR: Ref
Upper stalagmitic floor						
YC 26	4.4		(1)	4.2		(1)
Stalagmitic floor of ensemble IV						
YC 7	10.6	0.34	(1)	11.8	0.39	(4)
YC 18	6.1	0.40	(1)	7.8	0.36	(4)
Lower stalagmitic floor						
YC 62	11.4		(1)	10.8	0.32	(4)
YC 62	13	0.30	(2)			
DEB 82-3 (211 f1)	19.9	0.92	(3)	23.2 (f1 and f2)	0.33	(4)
DEB 82-3 (211 f2)	19.4	0.87	(3)			
DEB 82-5 (211 f3)	15.5	0.82	(3)			

+ED = equivalent dose. The ED to h_1 was determined after thermal redistribution of the h_2 and h_3 lines over h_1. (Yokoyama et al., 1981, 1982 a)

References: (1) this work; (2) Valladas, as cited in (4); (3) Debenham, 1983; (4) Yokoyama et al., 1983.

LENGEND OF FIGURES

Fig. 1 - Schema of YC26 showing the main stratigraphic units I (top) to IV (bottom), as well as TL and ESR samplings. Sample ATL was studied both by TL and ESR and the other 4 only by ESR. Sample III, from a dark level, was found unconvenient for ESR analysis due to clay contamination.

Fig. 2 - Natural thermoluminescence of a powdered sample from YC62 after dilute acetic acid treatment and distilled water washing. Triboluminescence affects the TL glow curve from 200C onwards. The three curves correspond to aliquotes (3mg each) of the same powder.

Fig. 3 - Glow curves for the TLN, TLN + 6.7 krads and TLA for a β-dose of 13.4 krads of sample YC7.

Fig. 4 - Glow growth curves for the 280C peak of samples YC5, YC7 and YC26. The TL measurements have been taken at the maximum of the peak.

Fig. 5 - Glow gowth curves for the 280C and 350C TL peaks of YC7. TL was measured at the maximum of either peaks.

Fig. 6 - Glow growth curves of the 250C and TL peaks of YC18.

Fig. 7 - Plateau-test for sample YC7, indicative of partial fading of the 280C peak,

Fig. 8 - Protocole of alternative γ-irradiation and ESR measurements showing the orientation of the sealed silica glass tube containing the powdered sample for a-ESR measurement, and b γ-irradiation.

Fig. 9 - EPR spectrum of YC26 II and YC26 ATL.

Fig. 10 - ESR spectrum of YC18, From left to right: natural ESR and its modifications after a linear heating (10C/sec) of up to 235C or 418C.

Fig. 11 - Isochronal heatings of sample YC18. The same powder was successively heated at each temperature for 30' before ESR measurement.

Fig. 12 - Isochronal heating of sample YC62 (see text).

Fig. 13 - Growth curve of the h_1 and h_3 ESR peaks from sample YC26 ATL.

Fig. 14 - Effect of isothermal annealing at 200C on the h lines height in sample YC18.

Fig. 15 - Comparison of the YC18 natural spectrum with the spectra after 8h, 16h and 24h isothermal heating at 200C.

SCHEMA OF SAMPLE YC26

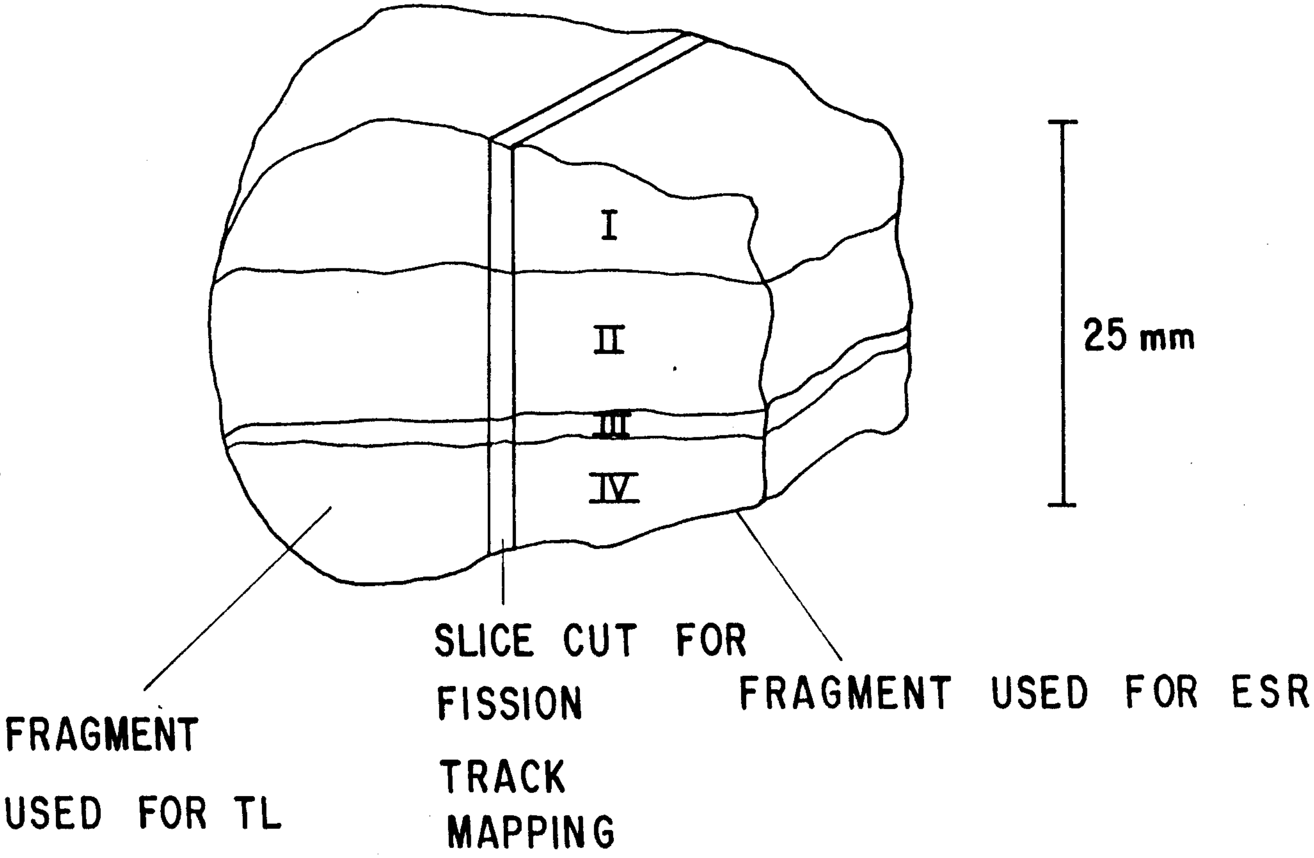

FIG. 1

CBPF-NF-013/84

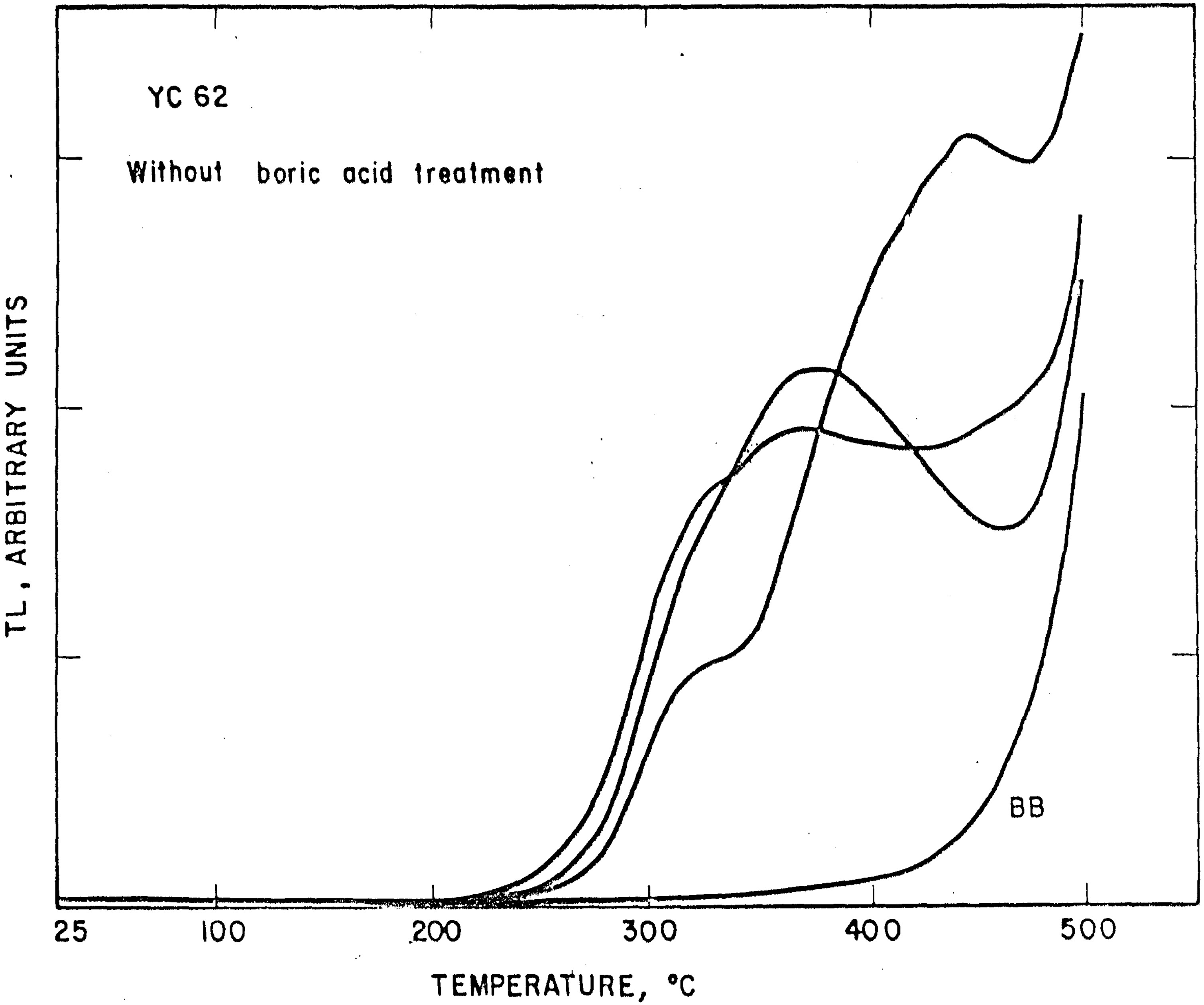

FIG. 2

CBPF-NF-013/84

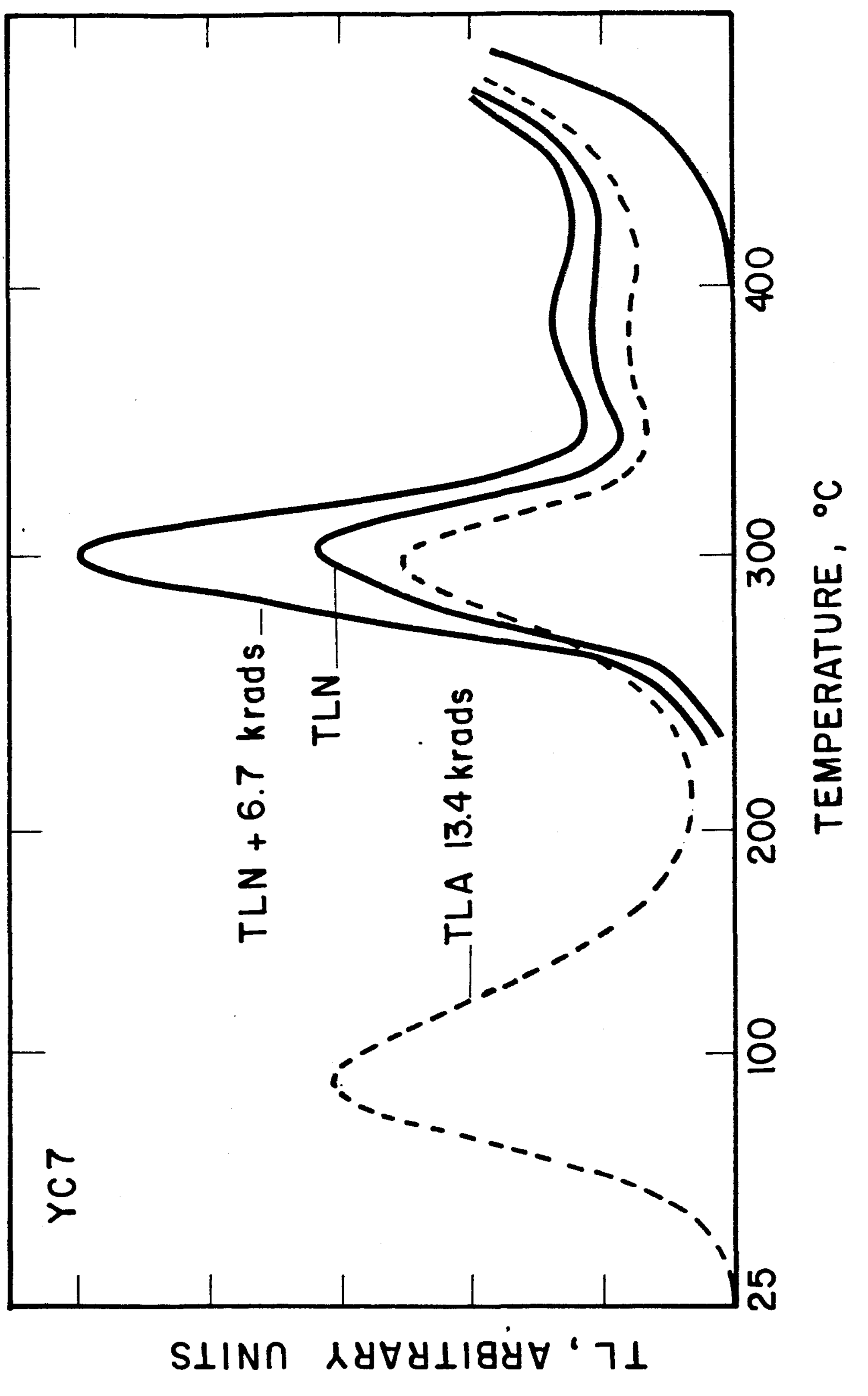
YC7
TLN + 6.7 krads
TLN
TLA 13.4 krads
25
100
200
300
400
TEMPERATURE, °C
TL, ARBITRARY UNITS

FIG. 3

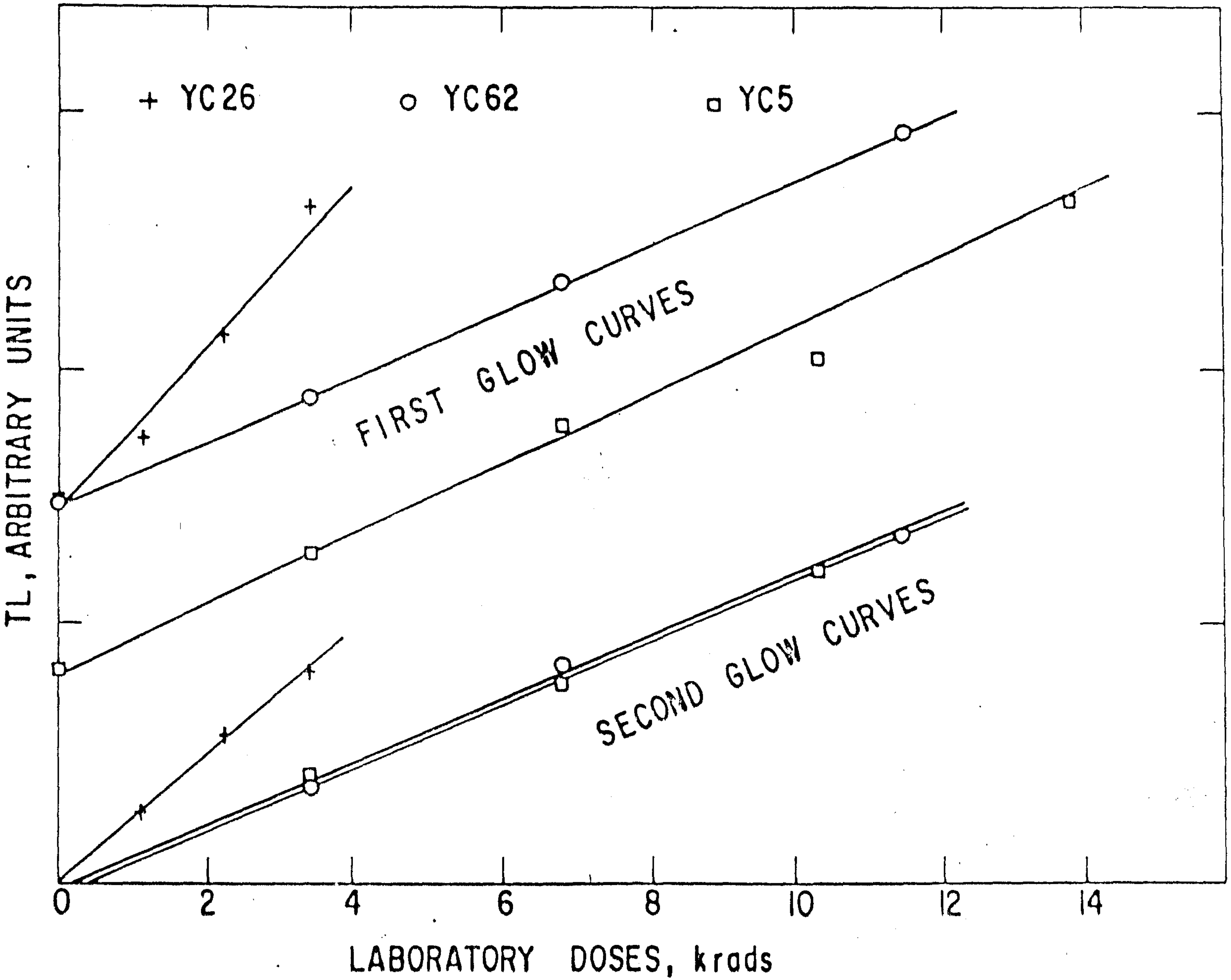

FIG. 4

CBPF-NF-013/84

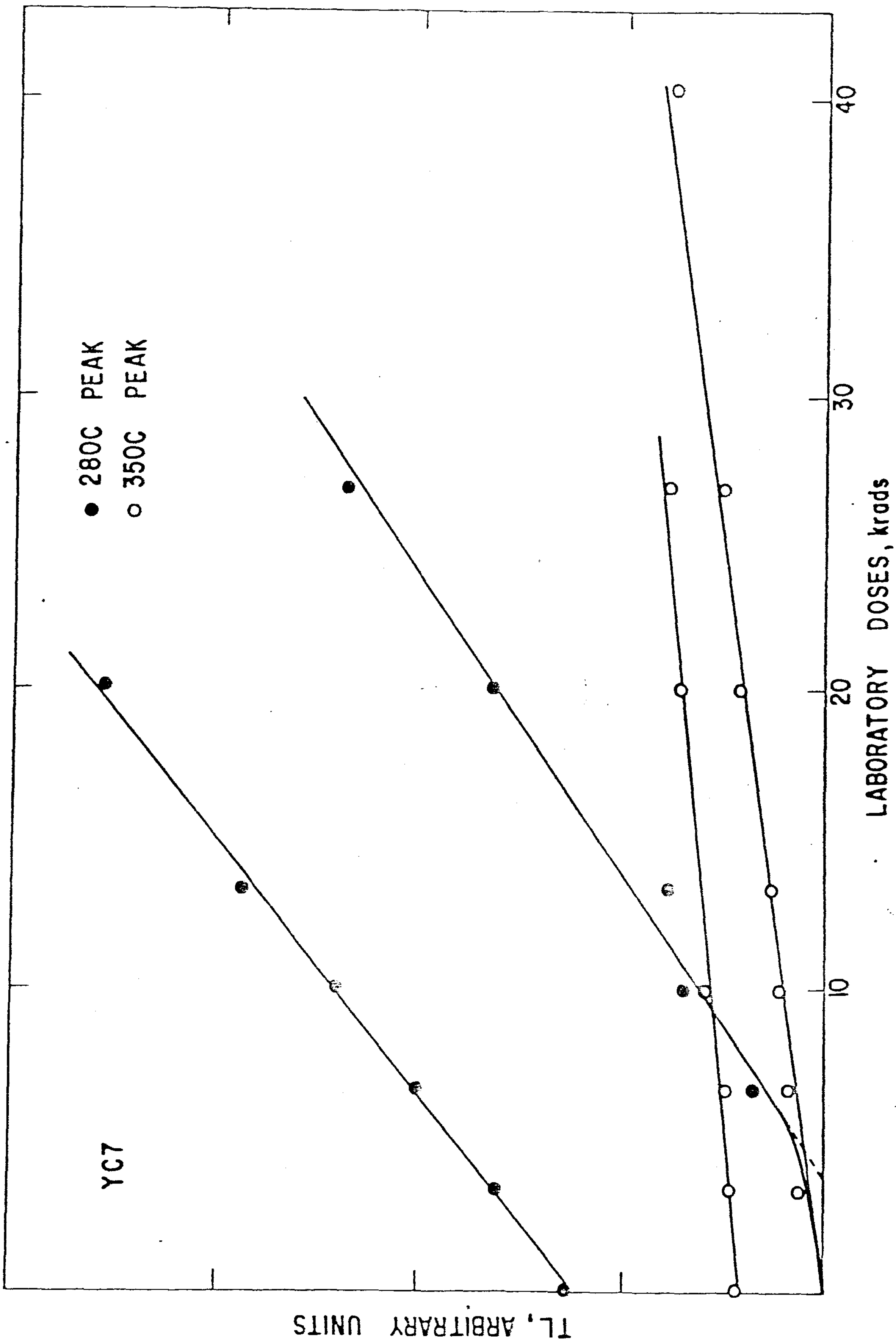
YC7
● 280C PEAK
○ 350C PEAK
TL, ARBITRARY UNITS
LABORATORY DOSES, krads
10
20
30
40

FIG. 5

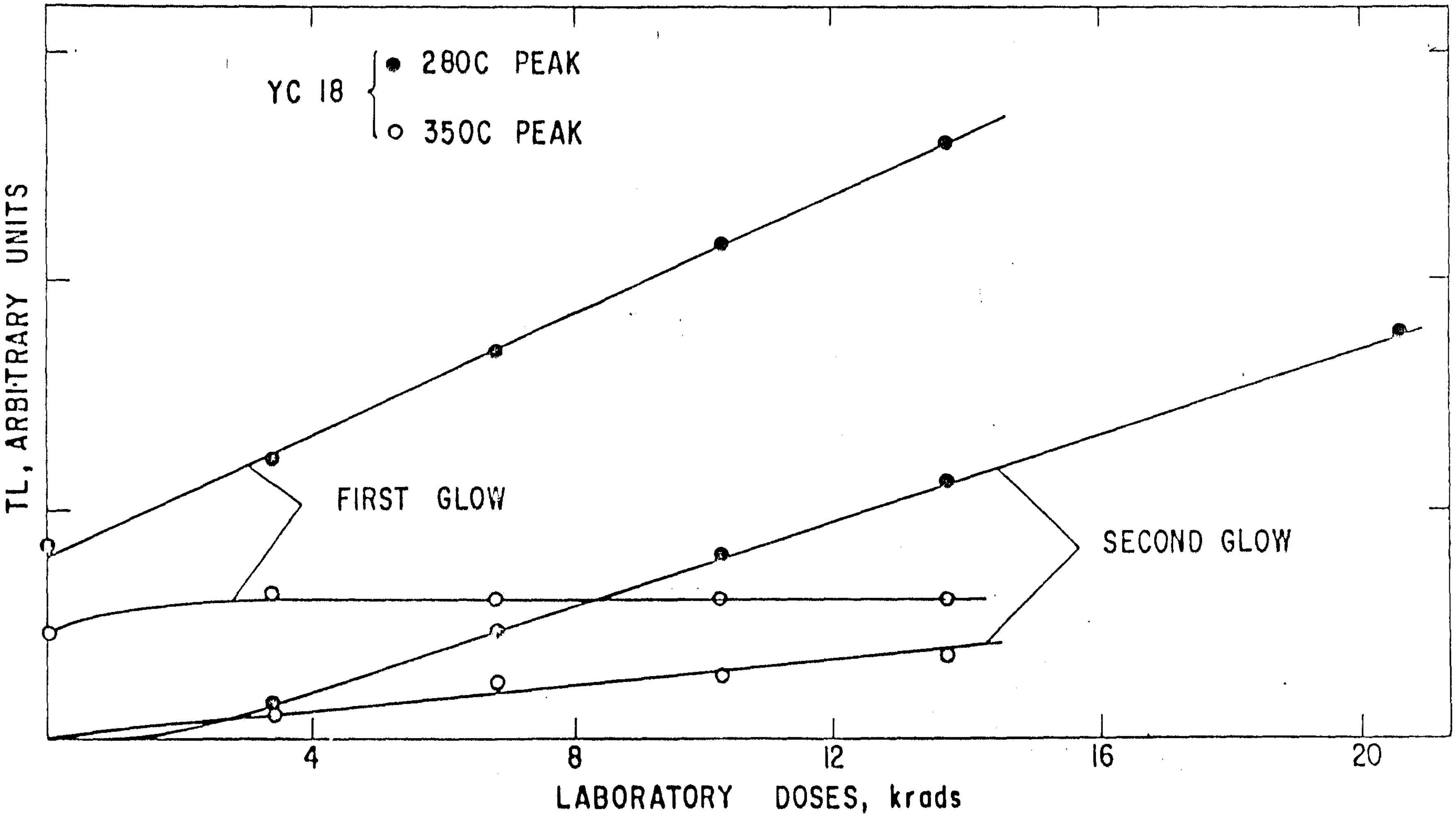
YC 18
280C PEAK
350C PEAK
FIRST GLOW
SECOND GLOW
TL, ARBITRARY UNITS
4
8
12
16
20
LABORATORY DOSES, krads

FIG. 6

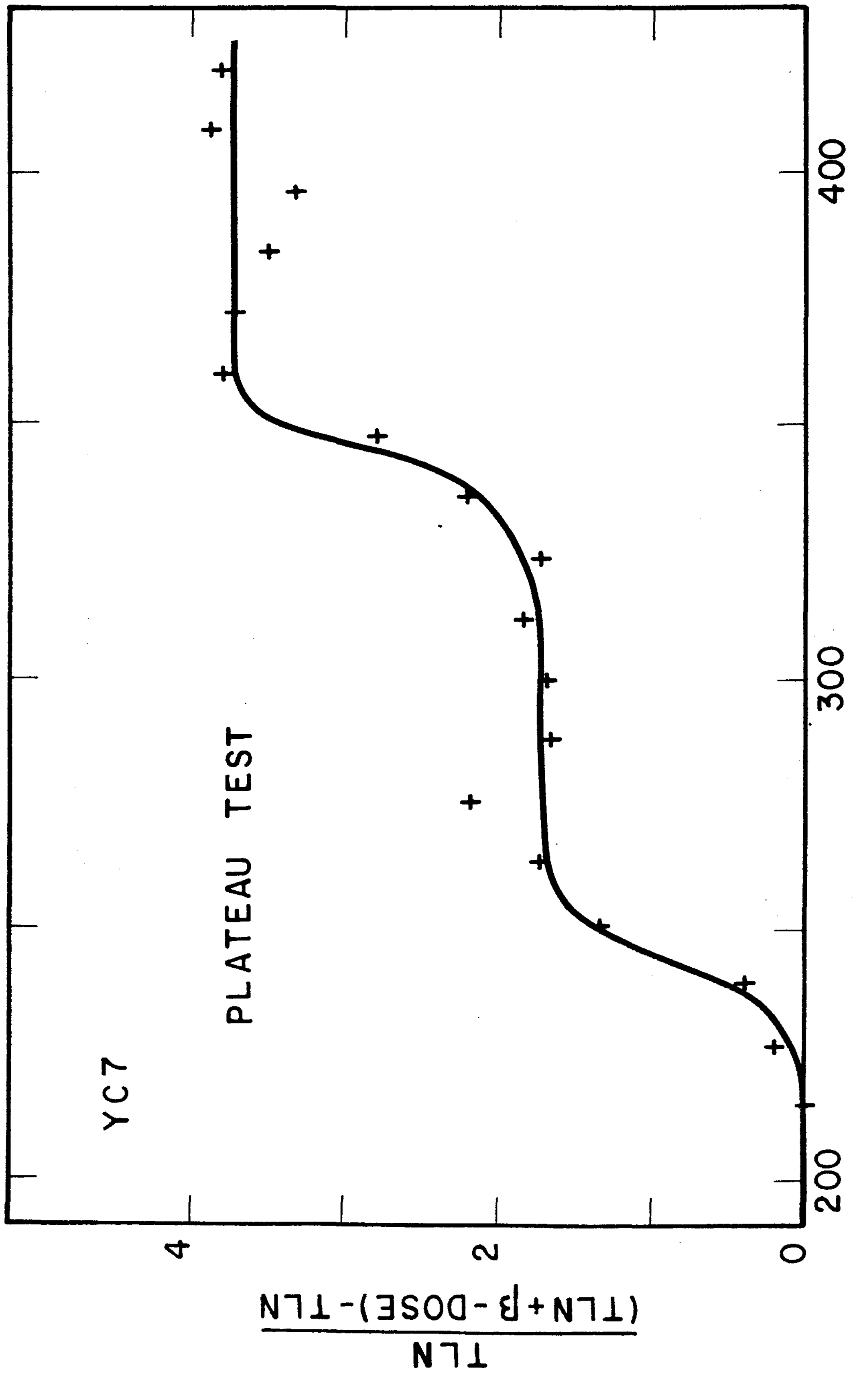

FIG. 7

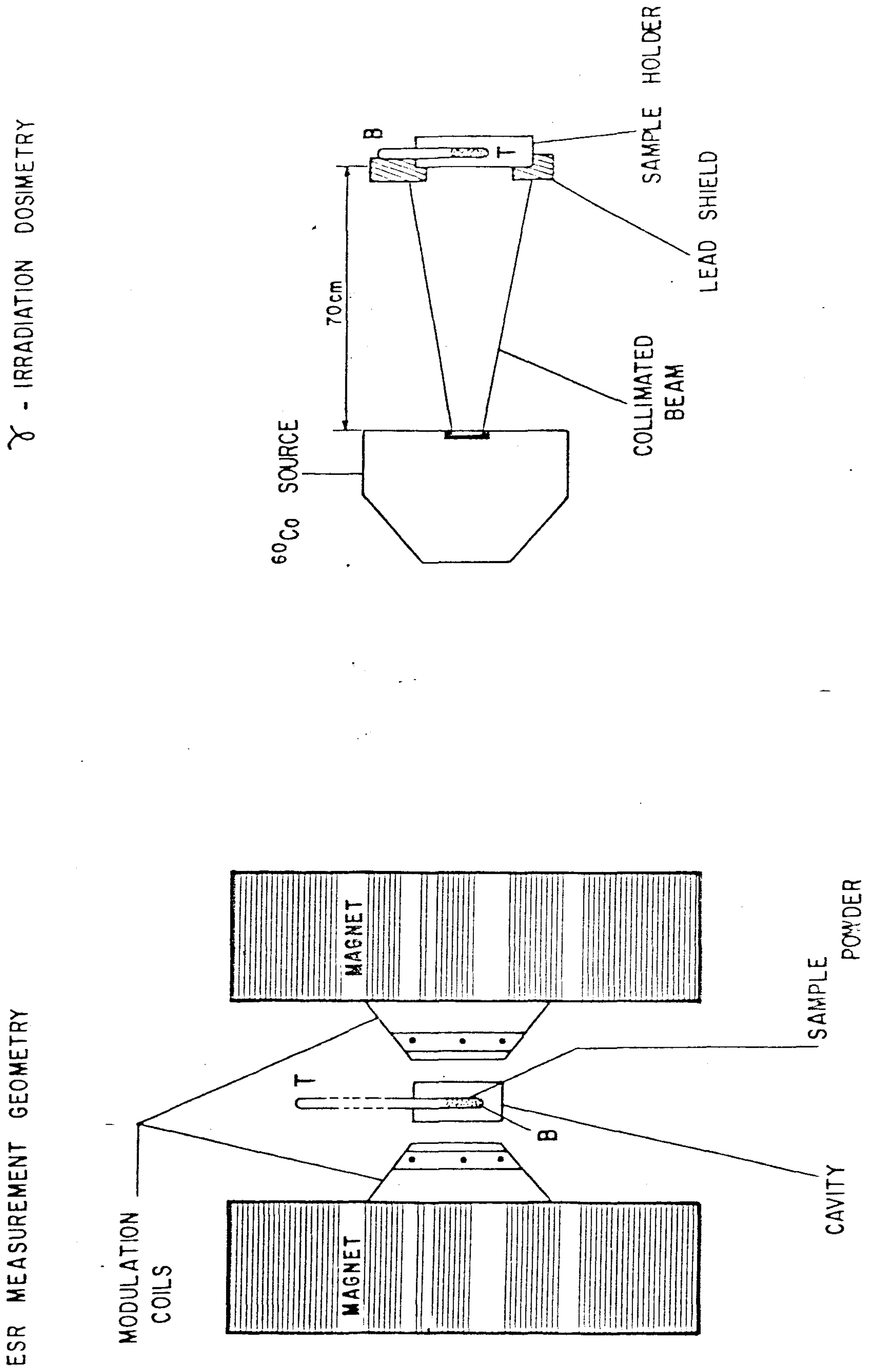
γ - IRRADIATION DOSIMETRY
70cm
B
T
SAMPLE HOLDER
LEAD SHIELD
COLLIMATED BEAM
^{60}Co SOURCE
(b)
ESR MEASUREMENT GEOMETRY
MODULATION COILS
MAGNET
MAGNET
T
B
SAMPLE POWDER
CAVITY
(a)

FIG. 8

EPR, ARBITRARY UNITS

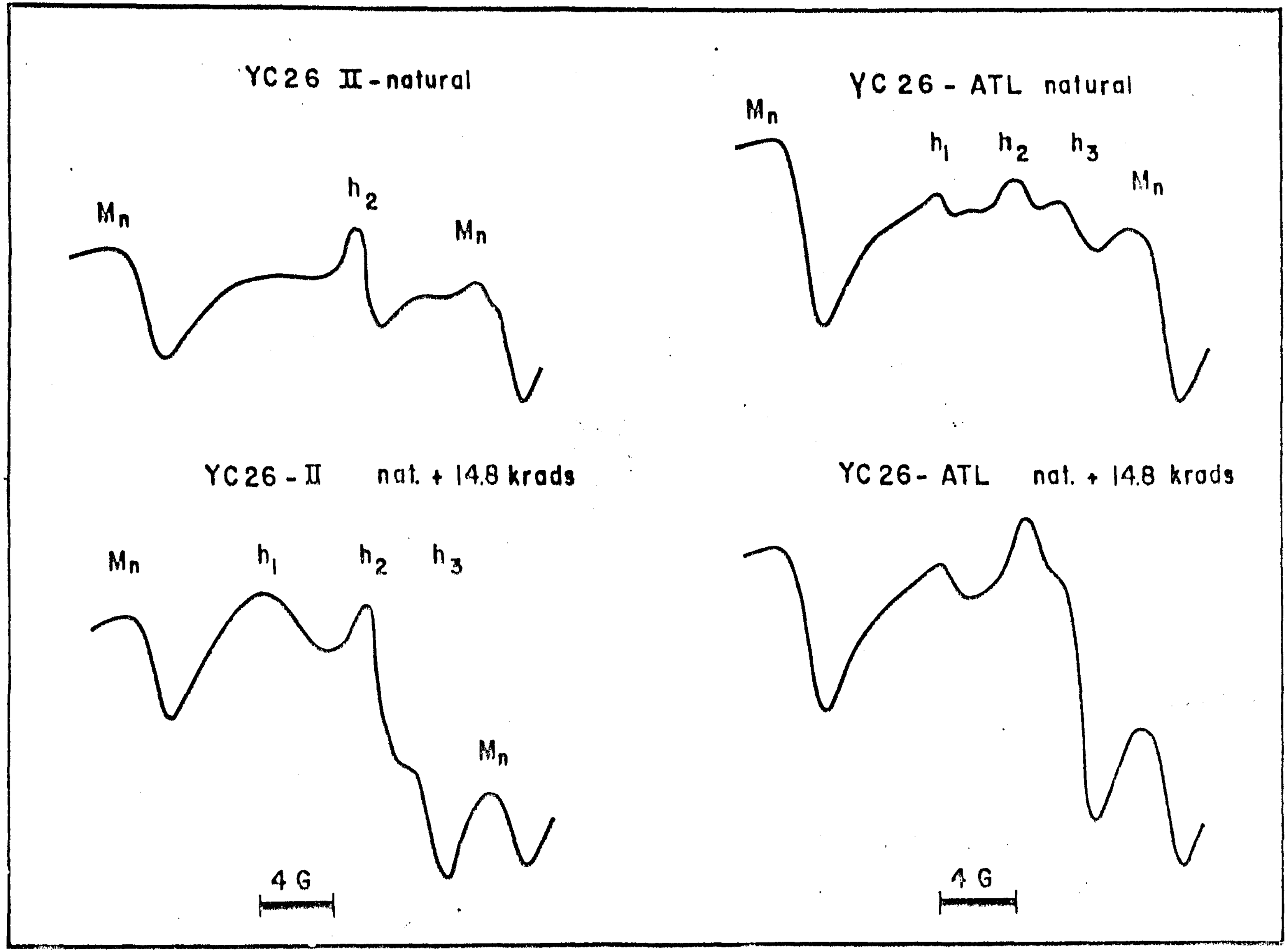

FIG. 9

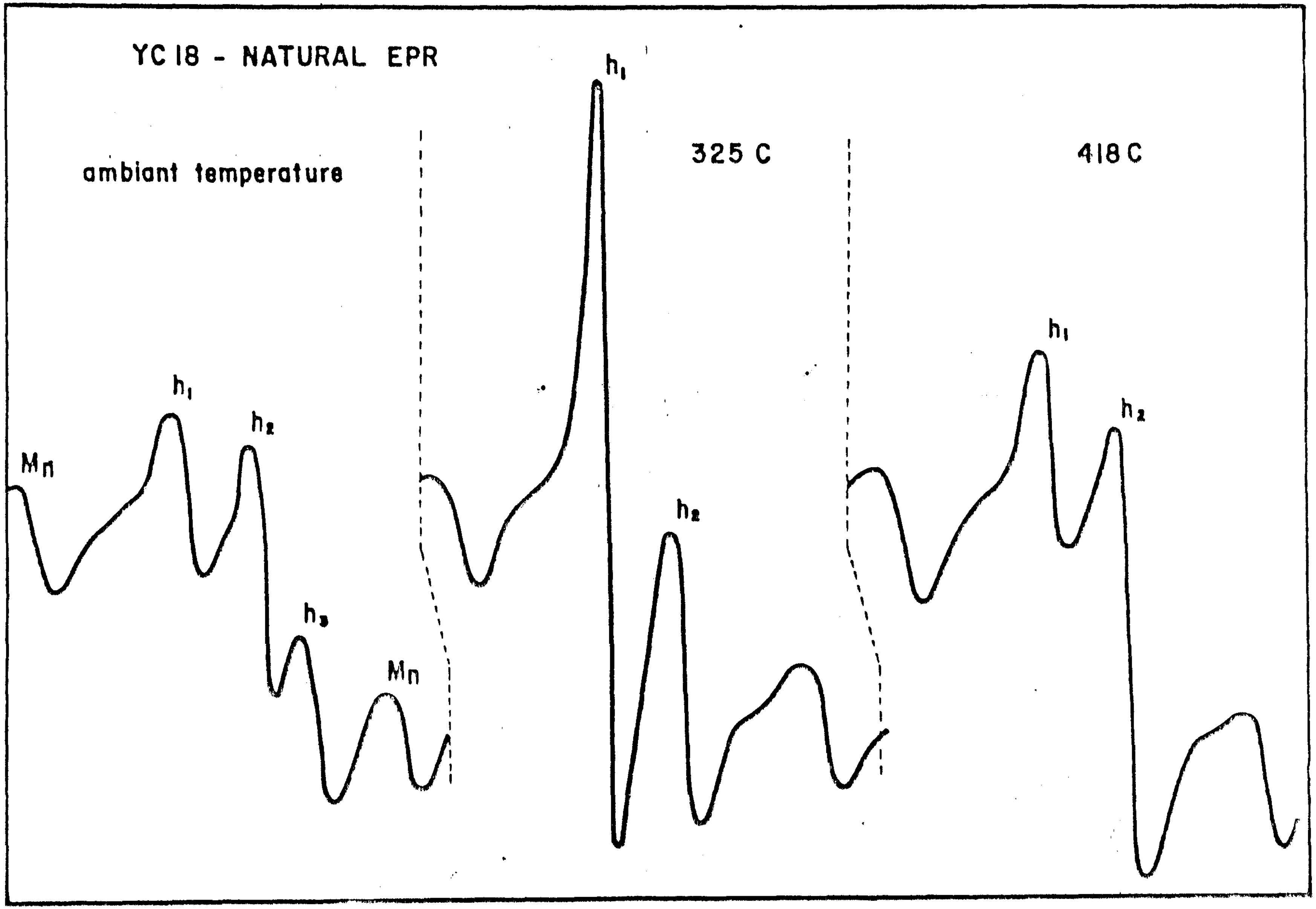
YC 18 - NATURAL EPR
ambiant temperature
325 C
418 C
Mn
h1
h2
h3
Mn
h1
h2
h1
h2

FIG. 10

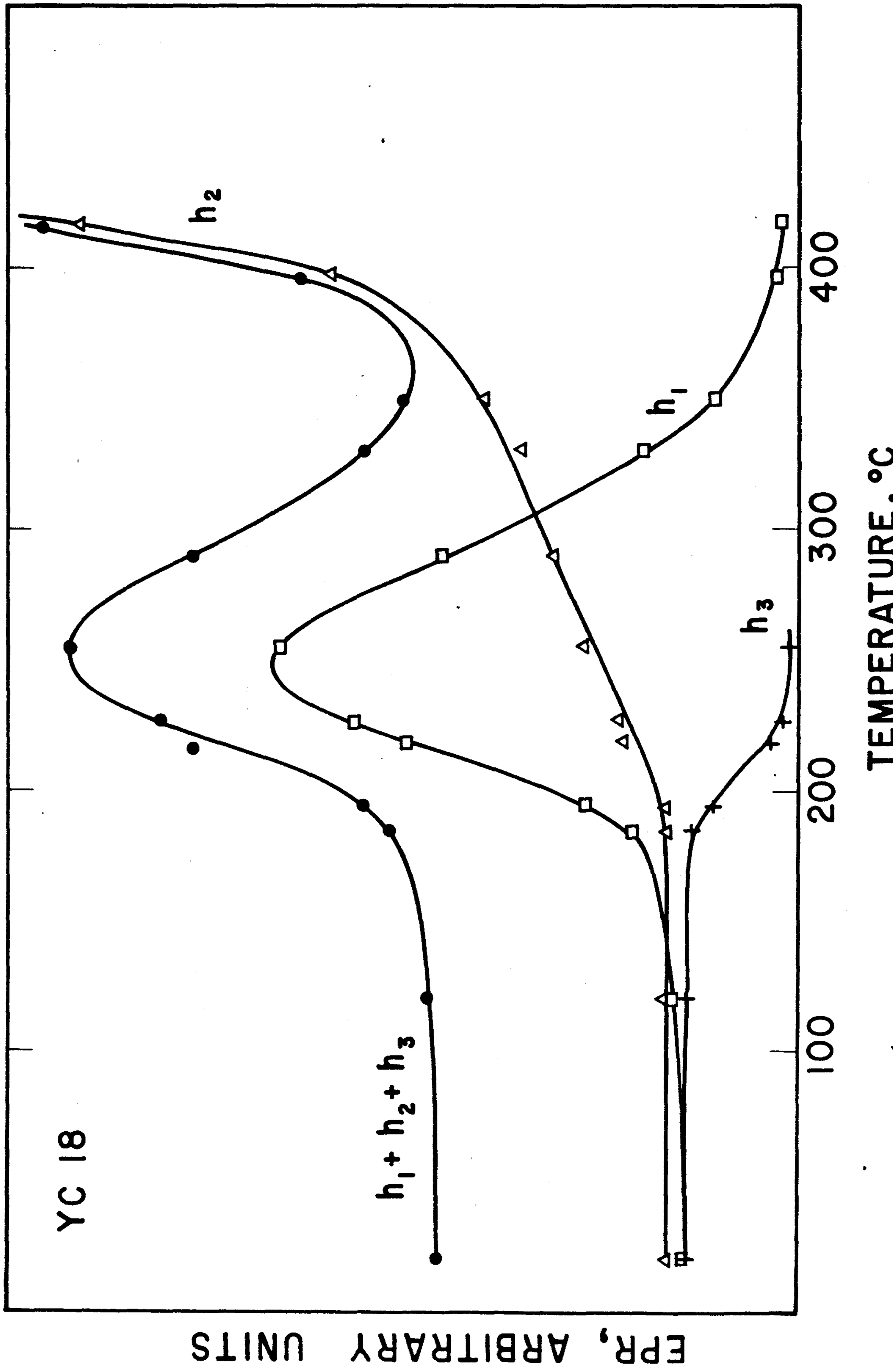
YC 18
$h_1 + h_2 + h_3$
h_1
h_2
h_3
100
200
300
400
TEMPERATURE, °C
EPR, ARBITRARY UNITS

FIG. 11

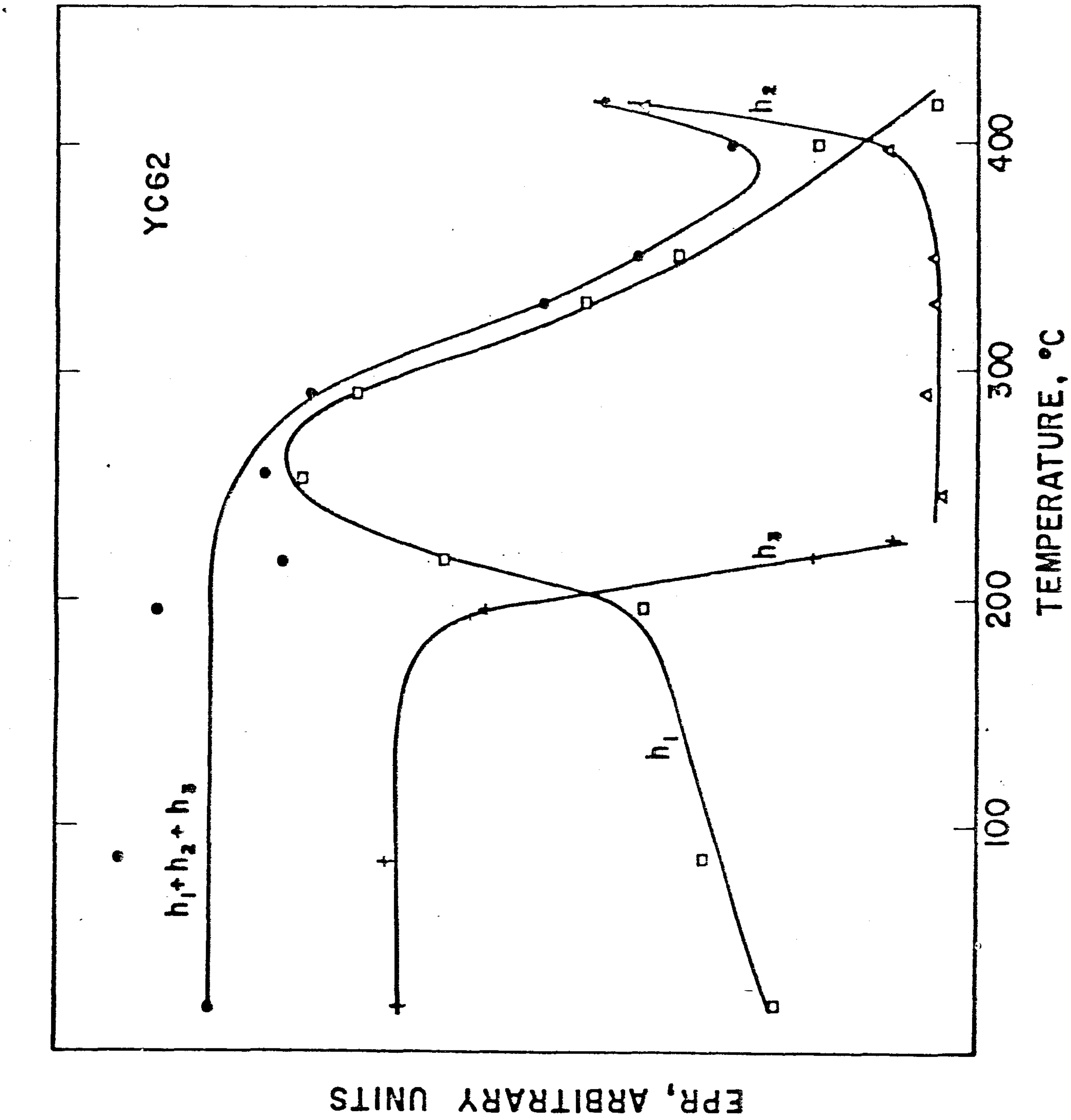
YC62
$h_1+h_2+h_3$
h_1
h_2
h_3
100
200
300
400
TEMPERATURE, °C
EPR, ARBITRARY UNITS

FIG. 12

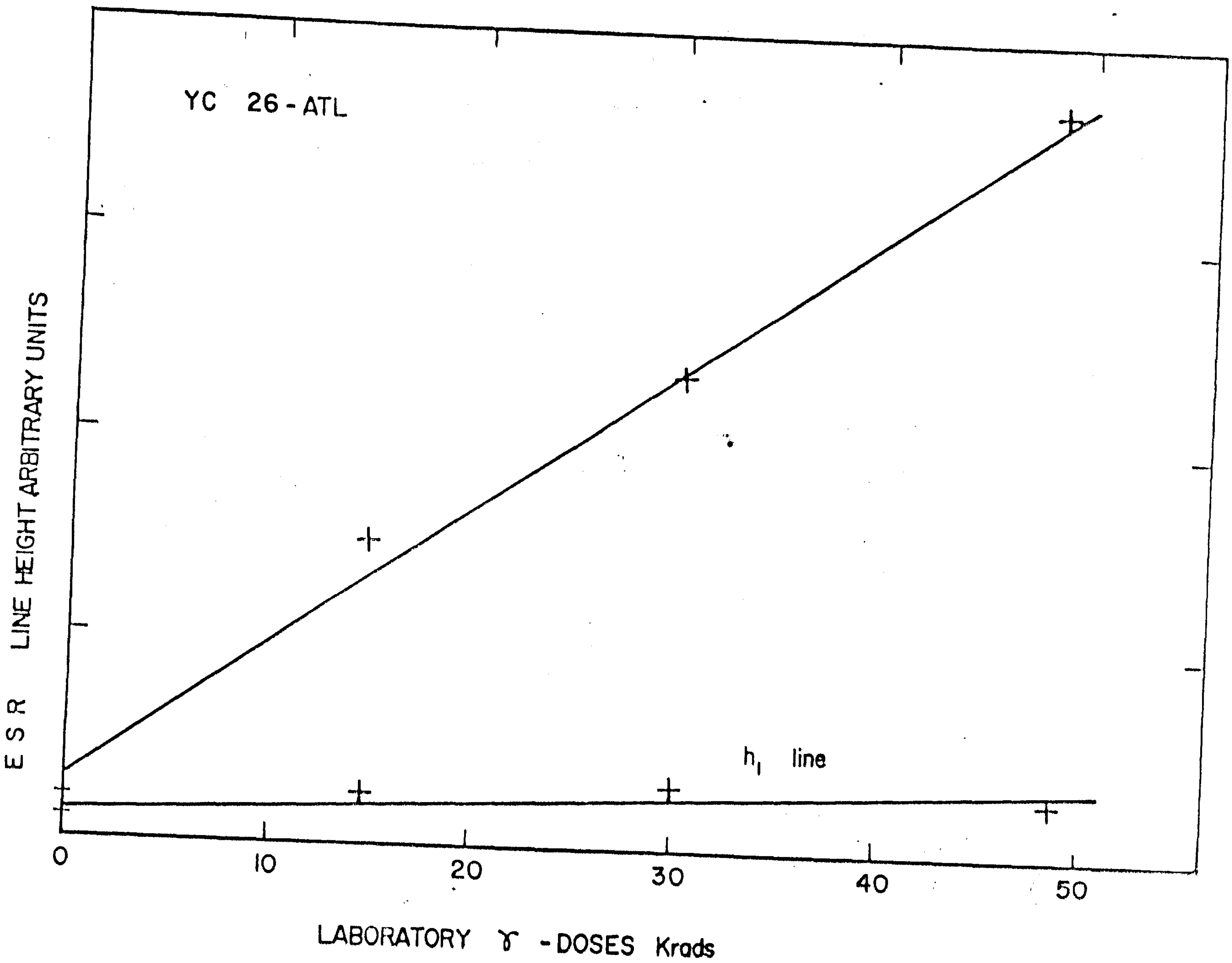
YC 26 - ATL
E S R LINE HEIGHT ARBITRARY UNITS
h₁ line
0
10
20
30
40
50
LABORATORY γ - DOSES Krads

FIG. 13

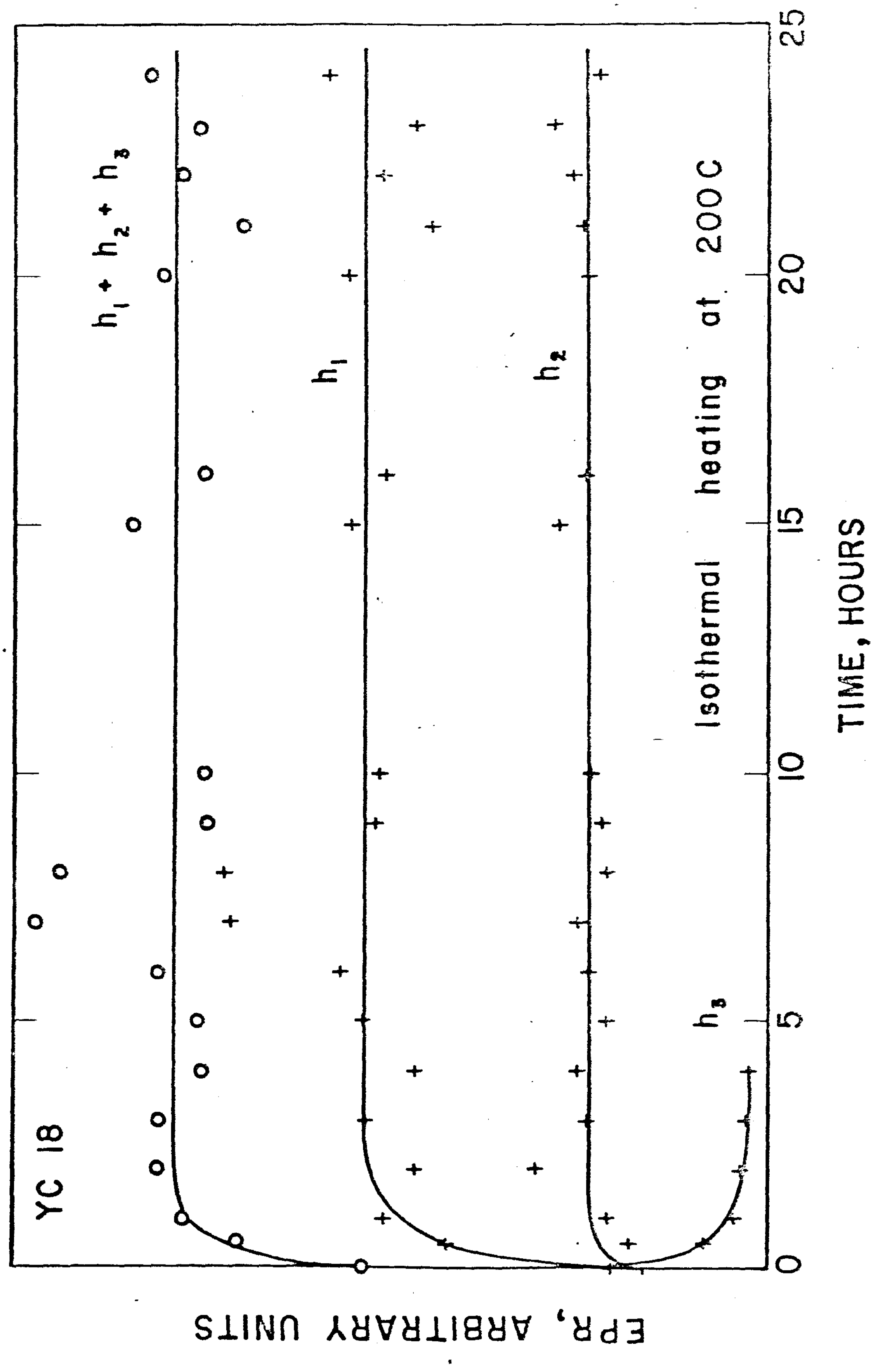
YC 18
$h_1 + h_2 + h_3$
h_1
h_2
h_3
Isothermal heating at 200 C
0
5
10
15
20
25
TIME, HOURS
EPR, ARBITRARY UNITS

FIG. 14

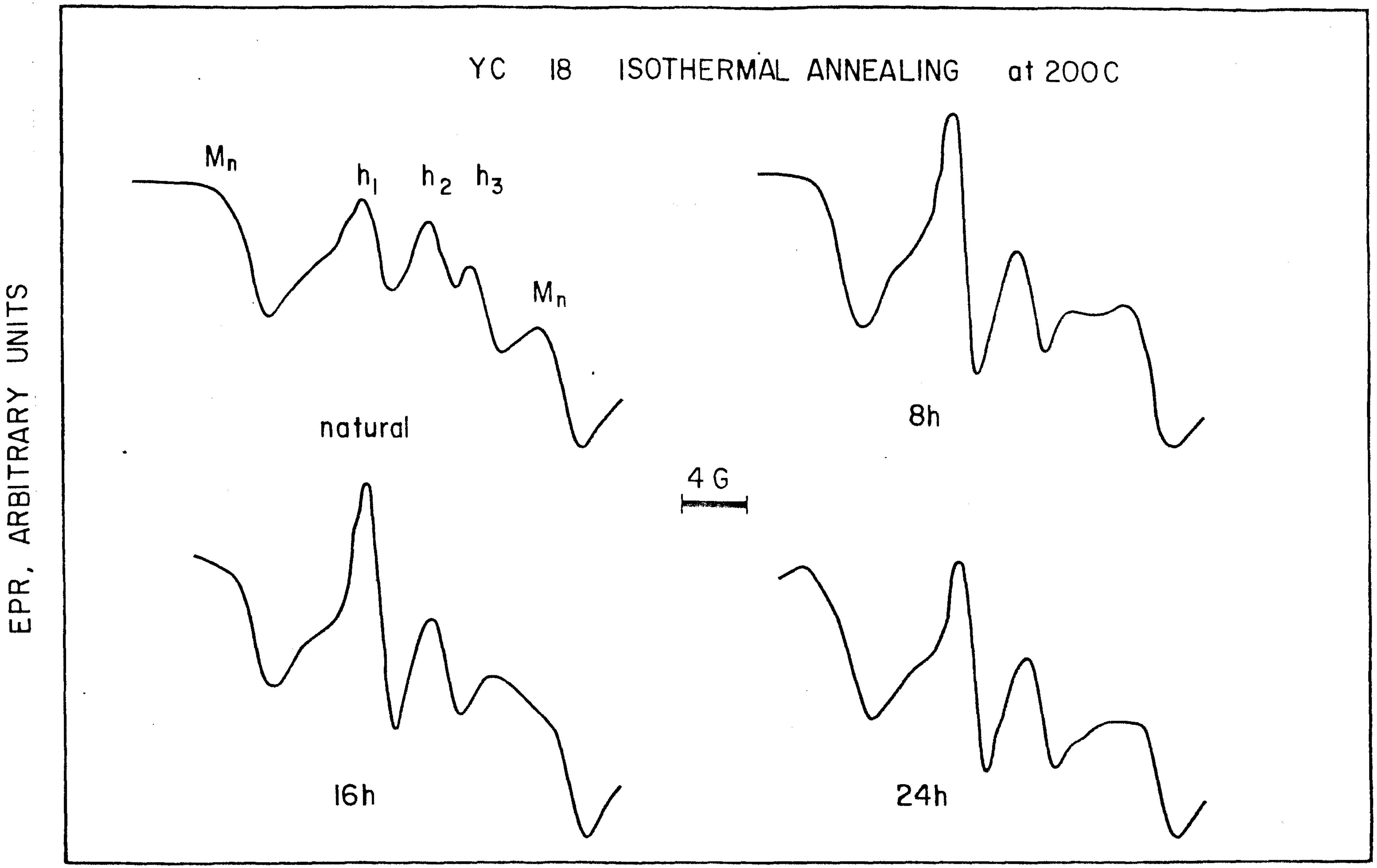
YC 18 ISOTHERMAL ANNEALING at 200C
EPR, ARBITRARY UNITS
Mn
h1
h2
h3
Mn
natural
8h
4 G
16h
24h

FIG. 15