ATTI ACCADEMIA NAZIONALE DEI LINCEI

CLASSE SCIENZE FISICHE MATEMATICHE NATURALI

RENDICONTI

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Thermoluminescence of some phosphorus-based compounds

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Serie 8, Vol. **42** (1967), n.6, p. 814–823.

Accademia Nazionale dei Lincei

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Chimica. — *Thermoluminescence of some phosphorus-based compounds* (*). Nota di Carlo Bettinali (**), Gastone Ferraresso (**) e Paolo Granati, presentata (***) dal Corrisp. G. Sartori.

Riassunto. — Vengono riportate le glow curves di fosfati cristallini del tipo MeH_2PO_4 aventi transizioni di fase note a bassa temperatura, di fosfati sodici aventi differenti rapporti Na/O, di composti in cui il fosforo è legato, oltre che all'ossigeno, anche ad atomi diversi come nel $POCl_3$. I dati ottenuti suggeriscono che: *a*) il processo luminoso non è legato alla formazione e distruzione di radicali ma a difetti o livelli metastabili preesistenti; *b*) l'intensità di termoluminescenza dei fosfati sodici è legata al numero di atomi di sodio per molecola; *c*) la termoluminescenza è drasticamente influenzata dal tipo di atomi legati al fosforo; *d*) i livelli metastabili responsabili della termoluminescenza, essendo stati metastabili della molecola, sono poco influenzabili dal tipo di catione e non influenzati dalle transizioni di fase.

INTRODUCTION.

The effects of radiations in inorganic phosphates have been the object of much research of different scopes such as: the researches related to inorganic PO_4^{--} and PO_3^{--} radicals in glasses and in crystalline systems [1–6]; the study of colour centers in phosphate glasses [7–10]; the study of phosphate materials for radiation dosimetry by means of thermoluminescence [11–13].

Recently the thermoluminescence of KH_2PO_4 was studied [14] but hypothesis on their origins was never previously made nor was it found if a relation between thermoluminescence and radicals formed from radiation or phase transitions exists.

In this paper are presented the experiments conducted on: crystalline phosphates of the type MeH_2PO_4, in which the low temperature phase transitions were previously known; on sodium phosphates with different Na/O ratios; and on compounds in which the phosphorus is bound not only to oxygen but also to different atoms such as in $POCl_3$ and in PCN.

EXPERIMENTAL.

The phosphates of the series MeH_2PO_4 were prepared by crystallization in bidistilled water from Merck reagent grade products, and/or prepared with reagent grade products. The phosphates of the sodium series were Merck reagent grade compounds or compounds obtained through thermal decomposition of NaH_2PO_4 and of Na_2HPO_4 [15].

(*) Comunicazione presentata al III International Radiation Research Congress – Cortina d'Ampezzo 26 giugno–5 luglio 1966.

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(***) Nella seduta del 21 giugno 1967.

Thermoluminescence measurements were made with a conventional instrument [16], using an E.M.I. 6255 S photomultiplier with low dark current. The samples were placed in a specially constructed cryostat, as described in previous paper [17], and subsequently cooled to liquid nitrogen temperature. The irradiation was supplied by an X–ray source (R. Seifert et Co.–Hamburg), having a flux of 8×10^4 R/min, when operating at 30 mA and 50 kV. The flux intensity on the sample was 3.85×10^3 R/min. The ESR spectrum of KH_2PO_4 was obtained with Hilgher-Watt Microspin instrument. All the samples were kept in a constant temperature furnace (105° C) until the moment of the use, to eliminate the water of crystallization and the atmospheric humidity on the surface of the samples.

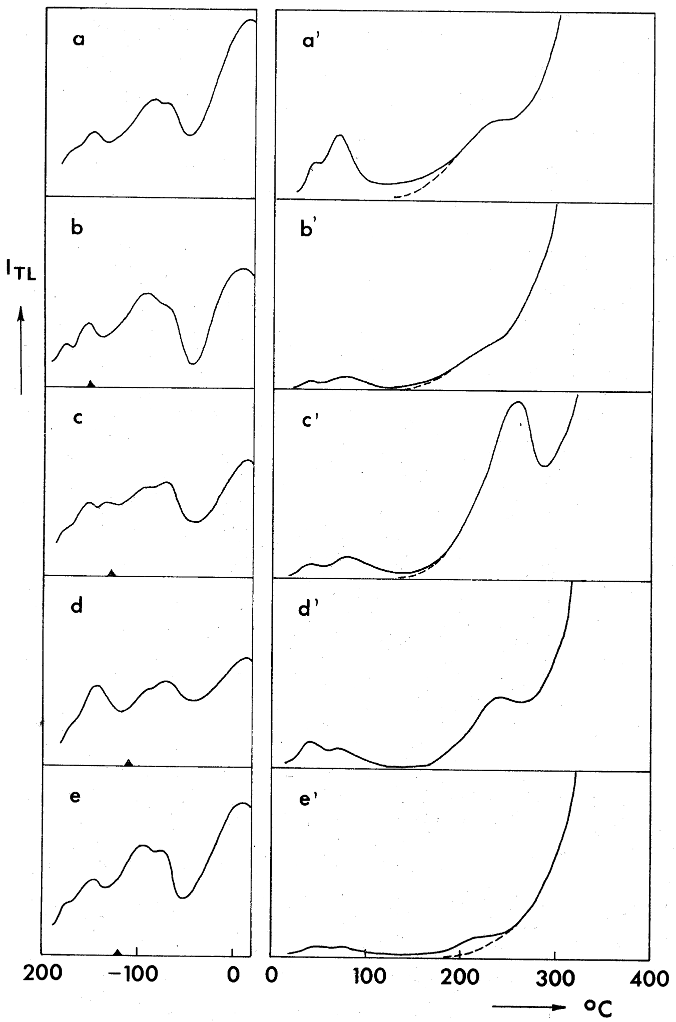


Fig. 1. – Glow curves of the series MeH_2PO_4:

a) NaH_2PO_4 This compound has no transition point; *b)* KH_2PO_4 – A peak roughly coincides with the transition point; *c)* RbH_2PO_4; *d)* CsH_2PO_4; *e)* $(NH_4)H_2PO_4$. In the compounds *c), d)* and *e)* any peak coincides with transition points. One can believe that the coincidence of the transition point with the peak at about −145° C in KH_2PO_4 is not significant.

RESULTS.

Fig. 1 shows the glow curves of the MeH_2PO_4 series where Me = = Na, K, Rb, Cs, NH_4. The triangular indices on the temperature axis indicate the points of ferroelectric transition for the potassium, rubidium and cesium phosphates, and the rapid variation of the dielectric constant for $NH_4H_2PO_4$ [18]. The part of the curves above 150° C can also be obtained from non-irradiated samples and is related to the thermal decomposition of the phosphates [19]. All the phosphates of this group, as can be seen from fig. 1, present three bands with peaks respectively situated around —150, —95 and 80° C temperature zones. The absolute and relative intensities of thermoluminescence were almost constant, varying little as the cations were varied, and the temperature of the peaks remained practically the same for all the phosphates of this series. As one can see from the figure, no peaks can be found to coincide with phase transitions.

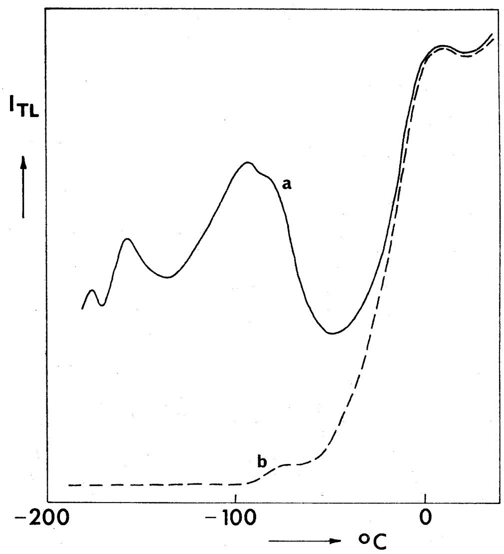


Fig. 2. – Glow curves of KH_2PO_4:

Curve a: sample irradiated at —190° C; *curve b*: sample irradiated at —140° C, warmed at —130° C for 10 minutes and recooled to —190° C. In the case b, radicals are still present but thermoluminescence before —140° C disappears. It is evident that no relation exists between thermoluminescence and radicals.

Fig. 2 indicates glow curves of KH_2PO_4 irradiated at —190° C (curve a) and irradiated at —140° C, warmed at —130° C, and allowed to remain at this temperature for ten minutes and subsequently recooled to —190° C (curve b). In the sample irradiated at —190° C a group of peaks around —150° C (curve a) occurs whereas if the same material is irradiated at —140° C this group of thermoluminescent peaks is not found (curve b); but the ESR signal, which some authors [6] attribute to the PO_3^- radical, persists. It is thus quite clear that if the radicals are responsible for the thermoluminescence, they should remain nonetheless undestroyed during the phase transition. Therefore, it can be said that no relation exists between the first group of thermoluminescent peaks and the recombination of radicals.

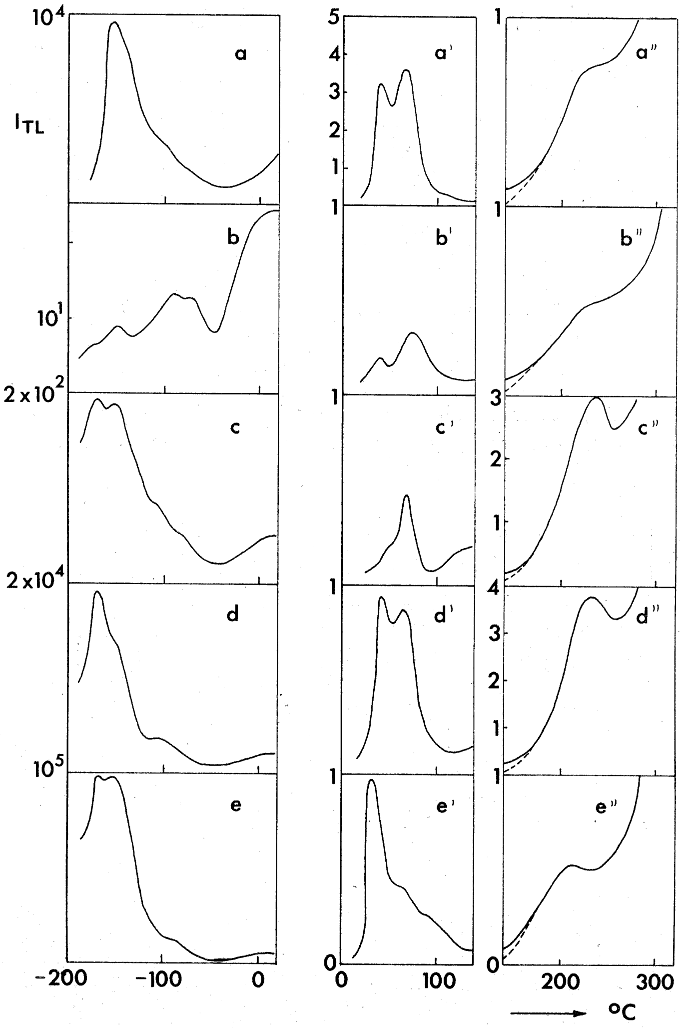


Fig. 3. – Glow curves of sodium phosphates series:

Curve a: $NaPO_3$; *curve b*: NaH_2PO_4; *curve c*: Na_2HPO_4; *curve d*: Na_3PO_4; *curve e*: $Na_4P_2O_7$. The common peaks have the same temperatures. The luminous intensity of the peaks around –150° C increases enormously. The increase of the other peaks is, on the other hand, very much less or almost nil.

Glow curves of the sodium phosphates series are shown in fig. 3. It should be noted here that the maxima of the glow curves have the same temperature for each sample. What varies enormously, however, is the intensity of thermoluminescence of the first group of peaks for equal radiation doses, as can be seen from the intensity units of fig. 3. The increase of the other peaks is, on the other hand, very much less or almost nil.

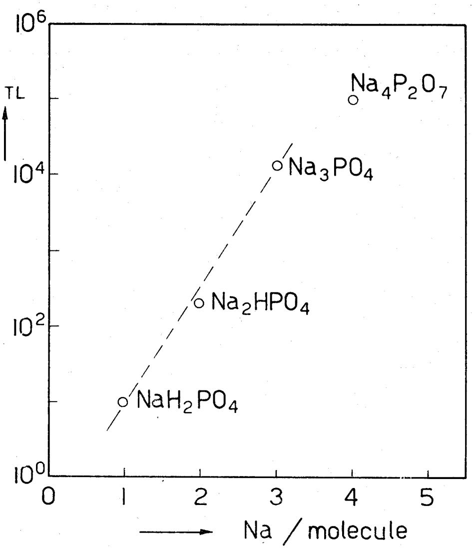


Fig. 4. – Increase of thermoluminescence intensity of the peaks around —150° C of the sodium phosphates series, as a function of the number of atoms per molecule.

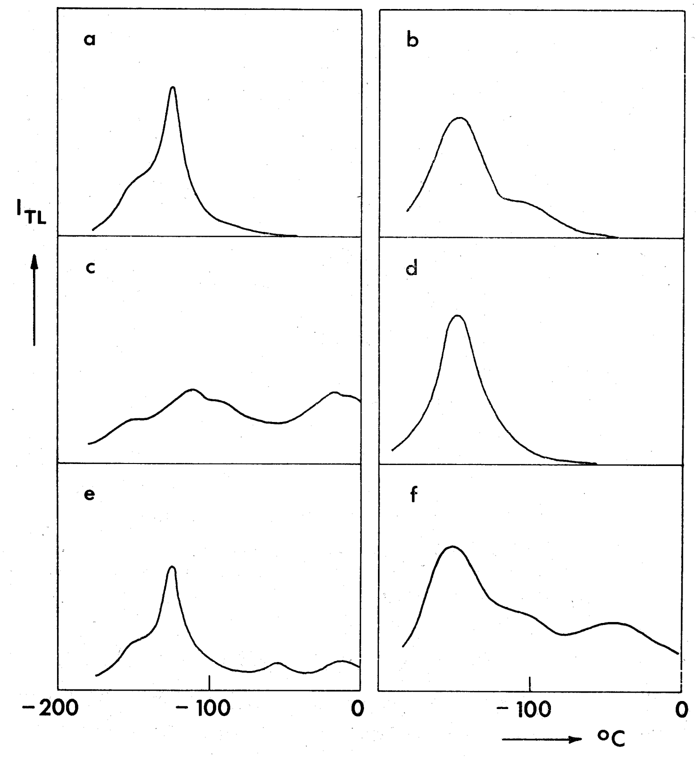


Fig. 5. – Glow curves of a series of phosphonitriles and of $POCl_3$

Curve a: $(RNCl_2)_3$ powder; *curve b*: $(RNBr_2)n$; *curve c*: $(RNCl_2)_3$ crystals; *curve d*: $P_3N_3Cl_3N\,(CH_2)_3$; *curve e*: $(RRNCl_2)_4$; *curve f*: $POCl_3$.

From fig. 4 one can easily observe the behaviour of the increase in luminous intensity of the peak at approximately —150° C with constant radiation dose as a function of the number of atoms of sodium per molecule.

Fig. 5 shows the glow curves of a series of phosphonitriles with different grade of polymerization, and containing also different anions, and of $POCl_3$.

Fig. 6 shows the behaviour of the thermoluminescence intensity of the peaks around —150° C as a function of the radiation dose, related to NaH_2PO_4. One can see that the thermoluminescence intensity reaches its maximum value with a dose of about 4×10^4 R. The formation of radicals continues instead for very much higher doses ($>10^6$ R). This leads one to believe that thermoluminescence is not connected to the presence of radicals but, on the contrary, to the pre-existing traps.

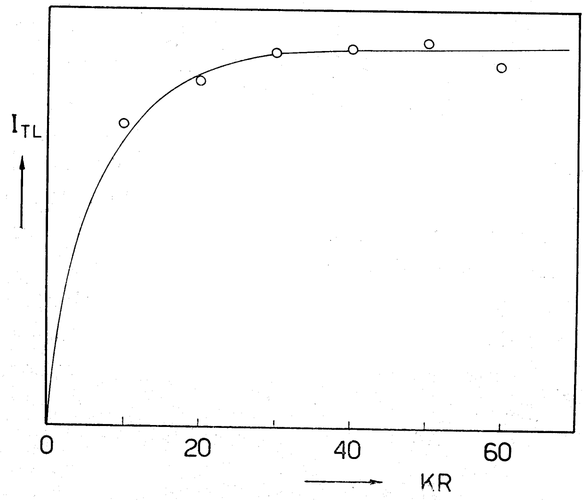


Fig. 6. – Thermoluminescence intensity as a function of radiation dose (related to NaH_2PO_4).

The luminous emission reaches its maximum value with a dose of about 4×10^4 R. The formation of radicals continues instead for doses very much higher ($> 10^6$ R). This leads one to believe that thermoluminescence is not connected to the presence of radicals but to the pre-existing traps.

DISCUSSION.

The thermoluminescence of irradiated compounds is due to different types of radiative recombinations but all connected in some way to the existence of a metastable level capable of entrapping electrons or holes. The postulated levels are as follows:

a) metastable levels of atoms or molecules [20, 21];

b) metastable levels created by impurities [21];

c) metastable levels related to unsaturated bonds on the surface or fluctuations of bond angles [23, 24];

d) levels due to lattice vacancies or to interstitial atoms or ions of thermodynamic origin or produced by radiation;

e) due to the presence of radicals.

Radiative emission can be stimulated by different mechanisms:

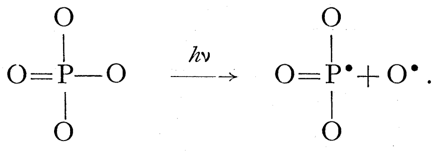
1) from the absorption of thermal phonons which excite electrons or holes trapped in the metastable levels from which they can return to the fundamental state giving off luminous emissions [21];

2) by destruction of metastable levels due to a phase transition [24, 25, 26] and consequent recombination of trapped species;

3) to recombination of radicals followed by a formation of excited molecules capable of giving off luminous transitions.

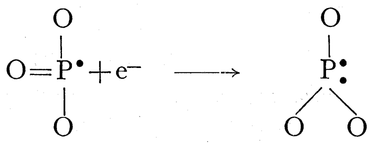
From the results obtained by ESR and by optical absorption (1–10) for the irradiated phosphatic compounds, two schemes were proposed:

A) Irradiation gives rise to a formation of oxygen vacancies according to the following scheme:



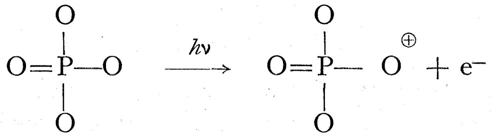
$$\mathrm{O{=}\overset{O}{\underset{O}{P}}{-}O} \xrightarrow{h\nu} \mathrm{O{=}\overset{O}{\underset{O}{P}}^{\bullet}} + \mathrm{O}^{\bullet}.$$

In the PO_3^{--} radical, the electron is in the sp level of the phosphorus atom. The radical can contain either a single unpaired electron or two electrons giving rise to paramagnetic and non-paramagnetic centers respectively. The stability of the radicals is conditioned to the possibility of the trapped oxygen to recombine with the PO_3^{--} group. A paramagnetic radical can, by capturing an electron, be transformed into a non-paramagnetic radical: such a hypothesis was previously postulated to explain the optical absorption at 6200 Å in metaphosphate glass.



$$\mathrm{O{=}\overset{O}{\underset{O}{P}}^{\bullet}} + e^{-} \longrightarrow \mathrm{\overset{O}{\underset{O\quad O}{P}}{:}}$$

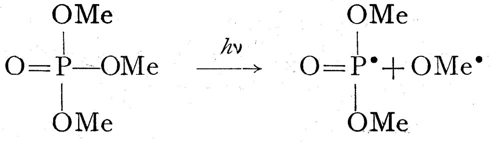
B) Irradiation causes the oxygen atom of the tetrahedron to lose one electron



$$\mathrm{O{=}\overset{O}{\underset{O}{P}}{-}O} \xrightarrow{h\nu} \mathrm{O{=}\overset{O}{\underset{O}{P}}{-}\overset{\oplus}{O}} + e^{-}$$

The stability of system is related to the activation energy of the trapped electron: that is, to the depth of the electron trap.

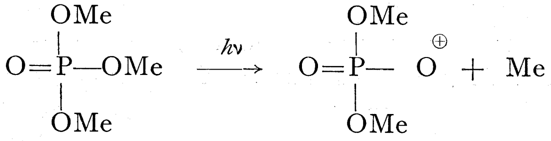
In the case where the phosphorus is related to the group OMe (Me = Li, Na, Rb, Cs) the reaction A would be



$$\mathrm{O{=}\overset{OMe}{\underset{OMe}{P}}{-}OMe} \xrightarrow{h\nu} \mathrm{O{=}\overset{OMe}{\underset{OMe}{P}}^{\bullet}} + \mathrm{OMe}^{\bullet}$$

Irradiation causes both the formation of the radical Me_2PO_3 with one unpaired or two paired electrons on the sp orbital of the phosphorus and the formation of a radical OMe. The stability of this system is related to the stability of the OMe radical [12].

Radicals can also be formed according to scheme B), that is, a hole trapped on an oxygen atom bound to the phosphorus and an electron trapped on the atom of the metal:



$$\mathrm{O{=}\underset{\displaystyle OMe}{\overset{\displaystyle OMe}{P}}{-}OMe} \xrightarrow{h\nu} \mathrm{O{=}\underset{\displaystyle OMe}{\overset{\displaystyle OMe}{P}}{-}\ \overset{\oplus}{O}} + \mathrm{Me}$$

The stability of this system is dependent on the activation energy of the trapped electron.

It is possible however to have a third type of process: C) the electron liberated by irradiation become trapped in the pre-existing centers. Such centers can be lattice vacancies and interstitial atoms or ions, or also internal metastable levels of the molecule, analogous to what happens in the Tl ion in KCl(Tl) and for the tetrahedral group WO_4^{--} of wolframites.

Experimental data seem to suggest that the electron traps are of the same type for all the phosphates of the series MeH_2PO_4. In fact the temperature of the peaks are common to all the glow curves and the intensity of these peaks seems to vary only slightly. However, in the case of the phosphates where the phosphorus is bound to atoms different from oxygen, the glow curves are drastically changed. In addition there seems to be a phase transition which does not influence the thermoluminescence of the phosphates: in fact, if such transformations give rise to the destruction of traps with consequent luminous emission of the electrons and holes, one should find once again a notable luminous emission at the transition temperature and obviously peaks at higher temperatures should not be found.

The series of sodium phosphates presents and interesting behaviour: for the first three terms of the series, NaH_2PO_4, Na_2HPO_4 and Na_3PO_4, the intensity of thermoluminescence peaks around -150° C increases from the first to the third term in the order of 10^1, 10^2 and 10^4 respectively. The other two terms $NaPO_3$ and $Na_4P_2O_7$ have respective intensities of 10^4 and 10^5 (arbitrary units).

The increase of intensity of the peak at -150° C of the sodium phosphates can be accounted for by:

(i) a greater probability of bond splitting and thus, if the thermoluminescence is related to radicals, there would be greater probability of formation of centers;

(ii) a lower energy of formation of the interstitial atoms or ions;

(iii) a hydrogen quenching effect;

(iv) a greater efficiency of the luminous process;

(v) a greater amount of pre-existing thermoluminescent centers.

Hypothesis i) may not be acceptible, keeping in mind the saturation curve which is valid, with small variations, for most of the phosphates studied. In fact, for doses of radiation that do not permit one to see the presence of radicals, thermoluminescence has already reached its maximum value. If the thermoluminescence were dependent on the number of radicals it should then increase for increased amounts of radicals produced by radiation. The same criterion is valid for the *hypothesis ii*): in fact it is not possible to think that with radiation doses higher than those related to thermoluminescence saturation, the number of interstitials would not increase. *Hypothesis iii*) might be possible but the mechanism is not known: it is an experimental fact however that the compounds containing hydrogen (NaH_2PO_4 and Na_2HPO_4) have an intensity of order 4 and 3 lower than the subsequent compound (Na_3PO_4) without hydrogen respectively and still lower than all the other terms without hydrogen ($NaPO_3$ and $Na_4P_2O_7$). *Hypothesis iv*) is without doubt possible but most improbable in this case for two reasons: firstly, identical sequences for both the increase in the sodium content and increase in impurities seem very improbable and secondly the experiments were performed with Merck products of different stocks and with Erba products both giving the same results. *Hypothesis v*) seems more convincing although it does not exclude hypothesis iii) and iv); in fact, supposing that the metastable levels are pre-existing and connected in some way to the presence of sodium and also that the principal effect of radiation is to fill these levels (and not to form them), then one can explain the dependence of the intensity of thermoluminescence from the number of atoms of sodium per molecule and the behaviour of the saturation curve.

There remains nevertheless the fact that the increase of luminous emission is too high to be justified solely on the basis of the number of metastable levels as a function of the increase in the number of sodium atoms. This fact could be explained by admitting also hydrogen quenching effect; for whenever the sodium increases, the hydrogen decreases. Such an hypothesis however is not supported by any known data.

CONCLUSIONS.

The curves of thermoluminescence between —190° C and +20 of the MeH_2PO_4 type phosphates present peaks at temperatures practically equal for all the cations. The sodium phosphates having different sodium contents show common peaks and other new peaks appear and increase with the increase on the Na/O ratio. One can see also the little or no variation of the glow curves of the sodium phosphates series between 20 and 400° C. Moreover the thermoluminescence intensity of the peaks around —150° C increases with the number of sodium atoms per molecule.

The thermoluminescent peaks between 20 and 400° C of the MeH_2PO_4 type phosphates are common for all the glow curves of the series, but their intensities are only slightly variable.

The data obtained for the KH_2PO_4 seem to exclude that the radicals are the agent responsible for the thermoluminescence. It seems, instead, from the extremely low value for the thermoluminescence saturation, that the process is not connected to the radicals but more likely to pre-existing defects or metastable levels.

If one considers the effect of phase transition of the examined compounds on thermoluminescence, the data obtained can only show that no relation exists between the point of transformation and the thermoluminescent peaks. The data seem to indicate that the metastable levels responsible for thermoluminescence, being the metastable states of the molecule, are only slightly influenced by the type of cation and not at all influenced by phase transition.

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