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Chimica. — *Behaviour of glow-curves during phase transitions in inorganic compounds.* Nota di CARLO BETTINALI (*), GASTONE FERRAROSSO (*) e JOHN W. MANCONI (**), presentata (***) dal Corrisp. G. SARTORI.

RIASSUNTO. — Sono state studiate le relazioni tra transizioni di fase e termoluminescenza in alcuni composti inorganici irradiati. Sono stati trovati tre casi tipici: A) la transizione di fase non influenza l'emissione luminosa; B) dà luogo ad un minimo di luminescenza a forma di cuspidi; C) dà luogo ad una brusca diminuzione dell'intensità luminosa, seguita da una leggera emissione luminosa o da nessuna emissione. Le variazioni dell'intensità di termoluminescenza sono state messe in relazione con una variazione dell'efficienza del processo luminoso dovuto all'incremento delle vibrazioni reticolari durante la transizione di fase. I picchi di termoluminescenza riscontrati da altri autori in composti organici sarebbero invece collegati alla migrazione di specie atomiche o molecolari cariche e loro ricombinazione con specie di segno opposto. I dati sperimentali sono interpretabili in base sia delle variazioni delle coordinate configurazionali del centro luminogeno nella fase iniziale ed in quella finale, sia della variazione della coordinata configurazionale dello stato eccitato (dovuta ad una supposta variazione della costante di forza) durante la transizione di fase.

INTRODUCTION.

In preceding works [1, 2] the authors have found that inorganic compounds showed a brusque and radical decrease in thermoluminescence emission if there existed a contemporaneous change of state. However if there is a corresponding solid-solid phase transition during the thermoluminescence emission one can note either a more or less brusque decrease in thermoluminescence emission or no variation at all.

The behaviour shown by organic compounds was different [3-11]: in coincidence with the phase transition there was observed an increase in the TL emission. This fact seems to present a co-relation between the mobilization of atomic or molecular ionized species and phase transition.

In this Note the Authors report the data obtained from some substances whose transition points were known previously: the $\text{H}_2\text{O}-\text{P}_2\text{O}_5$ system, sulfur, $(\text{NH}_4)_2\text{SO}_4$ and CsH_2PO_4 . The observed data are discussed on the basis of the configurational coordinate model.

EXPERIMENTAL.

The compounds used were reagent grade products from different origins (Merck, C. Erba) and of different stocks. In this way the Authors were able to evaluate the effects of impurities in the observed phenomena. In Table I

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(***) Nella seduta del 9 dicembre 1967.

the studied compounds are listed (column a), along with their transition temperatures (column b) and the corresponding type of transition (column c).

TABLE I.

Materials	Phase transition temp.	Phase transition type
H ₃ PO ₄ with 5% H ₂ O . . .	— 78	Glass-liquid
H ₃ PO ₄ with 10% H ₂ O . . .	— 84	Glass-liquid
H ₃ PO ₄ with 17% H ₂ O . . .	— 89	Glass-liquid
H ₃ PO ₄ with 27% H ₂ O . . .	— 95	Glass-liquid
H ₃ PO ₄ with 37% H ₂ O . . .	— 105	Glass-liquid
Sulfur (Rhomboidric)	+ 95.5 (r.m.); + 119 (m)	Rhomb. → mon. → liq.
(NH ₄) ₂ SO ₄	— 50	Rotational
CsH ₂ PO ₄	— 125	Ferroelectric

(*) Determined by DTA apparatus.

The experiments conducted in the temperature interval between — 180 and + 20°C were done with the cryostat described in previous works [12, 13] and partially sketched in fig. 1. Using this cryostat it was possible to perform the glow curves and differential thermal analysis (DTA) contemporaneously.

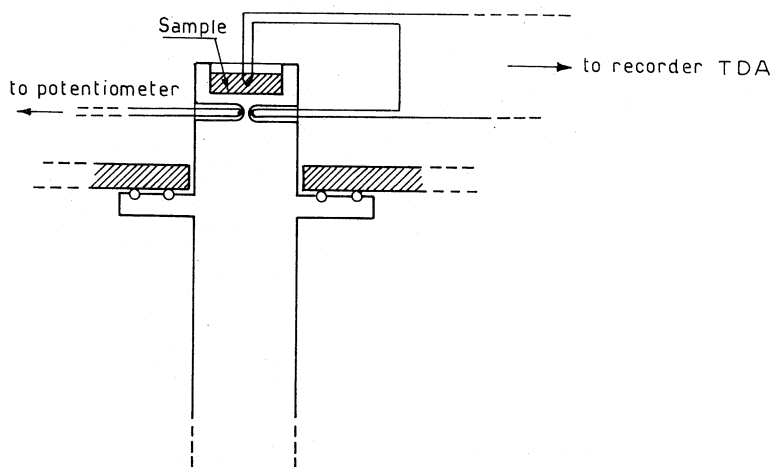


Fig. 1. — Sketch of the thermal rod of the cryostat.

One can see the position of the thermocouples of DTA.

The thermocouple of DTA (see fig. 1) was covered with a thin film of perspex, to avoid any possible corrosion during its immersion in the sample. The DTA signal was registered by a Sargent model SR recorder having a 1 mV full scale while the temperature was measured by a SAE 10757 potentiometer. The heating rate chosen was 10°C per minute.

The experiments conducted between 20 and 300°C were effectuated with a heating plate of constant heating rate in the interval of temperatures under study.

As a check, the DTA was also conducted with a Netzsch DTA apparatus.

All thermoluminescence measurements were taken by a conventional apparatus previously described [12]. Luminous emissions were detected by an EMI 6255 S photomultiplier of low dark current.

RESULTS.

Fig. 2 shows the glow curve of a sample of the $\text{H}_2\text{O}-\text{P}_2\text{O}_5$ system corresponding to H_3PO_4 with 15 % of H_2O (curve *a*); curve *b* is the DTA curve relative to the same sample. Comparing the glow curve with the DTA curve

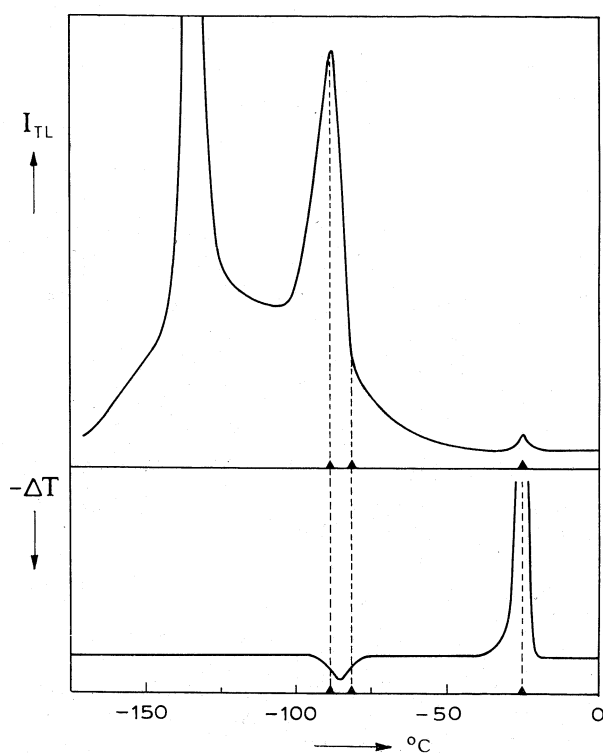


Fig. 2. - Glow-curve and DTA curve of H_3PO_4 with 15 % H_2O . One can see the coincidence of thermoluminescence breakdown with DTA endothermic peak and also the coincidence of the small thermoluminescent peak with the strong DTA exothermic peak corresponding to formation of the crystals.

it is possible to observe a definite breakdown of intensity in coincidence with the endothermic maximum relative to the liquid-crystal transition, there exists a large exothermic DTA peak and a thermoluminescent peak in the form of a cusp of modest intensity. One should also note the persistence of a constant and modest thermoluminescence intensity even in the liquid phase.

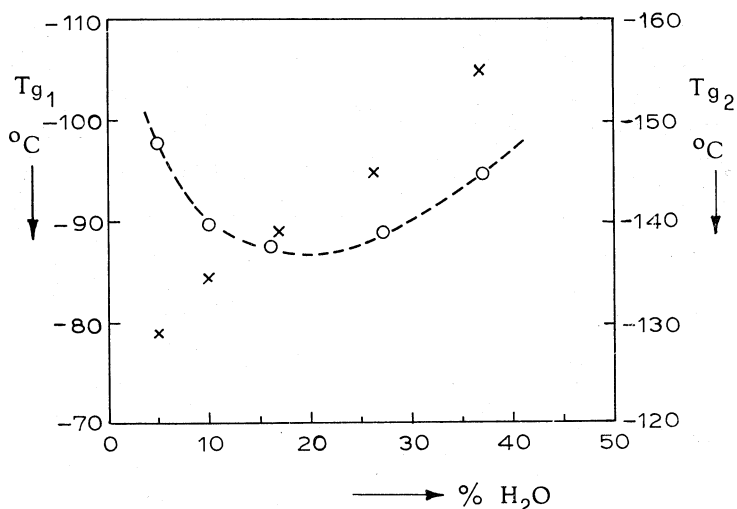


Fig. 3. — The crosses indicate the temperature of the thermoluminescence breakdowns of a series of samples of H_3PO_4 having an increasing content of H_2O . The circles indicate the temperatures of the first peak of the glow curve.

In fig. 3 one can see how the temperatures of the thermoluminescent breakdowns vary in function of the composition and then with the glass point temperatures. This fact confirms the relations existing between thermoluminescence breakdowns and phase transitions.

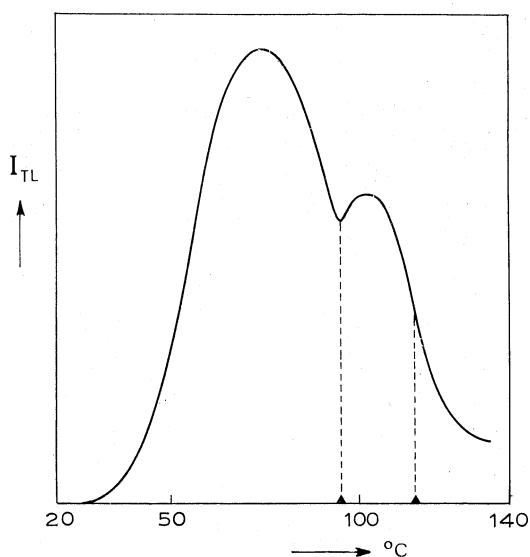


Fig. 4. — Glow curve of elemental sulfur—the existence of a cusp-shaped minimum at about 96°C and a subsequent thermoluminescence breakdown is evident.

Fig. 4 shows the glow curve of sulfur. Two phase transitions are present: solid-solid and solid-liquid. Passage from the rhombic phase to the monoclinic phase is characterized by a small minimum in the shape of a

cusps whereas transition from the monoclinic to the liquid phase gives a strong breakdown. The slope of this breakdown is less than that encountered in the other samples. This smaller slope is probably due to the low thermal conductivity of sulfur which leads to a retarded fusion of those grains which are not in direct contact with the heated metallic surface.

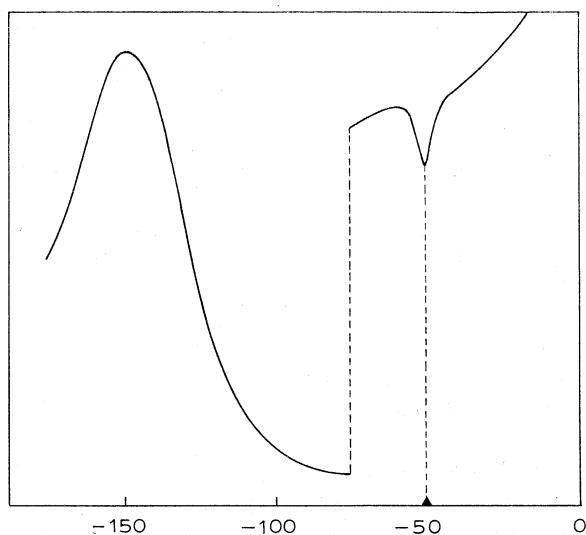


Fig. 5. – Glow curve of $(\text{NH}_4)_2\text{SO}_4$. The existence of a cusp-shaped minimum at the phase transition temperature is evident.

Fig. 5 shows the glow curve of the ammonium sulfate sample between -180 and $+20^\circ\text{C}$; the DTA curve has not been presented because of the insufficient sensitivity of our apparatus. Even in this case the solid-solid type transition was characterized by a cusp-shaped minimum.

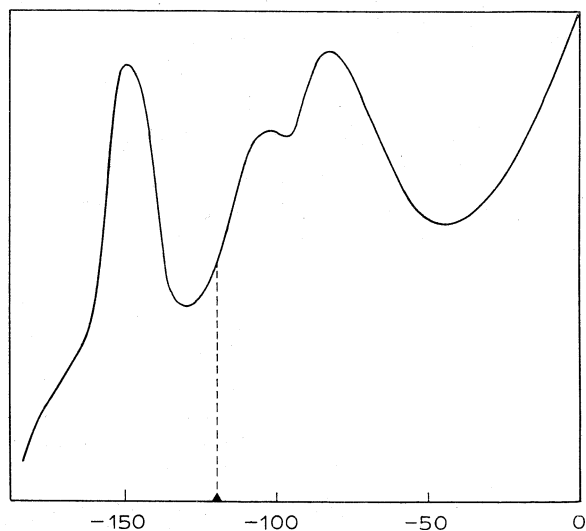


Fig. 6. – Glow curve of CsH_2PO_4 . No characteristic variation is present at the phase transition temperature.

In fig. 6 the glow curve of CsH_2PO_4 is shown. The phase transition occurred at -125°C and was not characterized by any brusque variation of the luminous intensity.

DISCUSSION.

In order that an interpretation be given to the experimental data, it is necessary that one discuss firstly what effect a phase transition can have on the behaviour of a glow curve. In the case of thermoluminescence which is due to a recombination of electrons trapped in a single level with ionized positive centers which are greater in number than the number of electrons in the conduction band, one has then that [14]:

$$(1) \quad I(T) = N_0 S \exp(-E_t/kT) \exp\left[-\int_{T_1}^T S \exp(-E_t/kT) \frac{dT}{\beta}\right]$$

where N_0 is the initial number of trapped electrons, E_t is the activation energy necessary for extraction of the trapped electrons, S is a frequency factor and β is the heating rate. Such an equation as the above presupposes that the efficiency of the luminous process be constant in the range of temperatures of the glow curve. But such an assumption is not always justified: in fact the efficiency of a luminous process is a function of temperature and is generally expressed by the equation

$$(2) \quad \eta = \frac{1}{1 + C \exp(-E_t/kT)}$$

where η indicates the efficiency of the luminous process, E_t is the activation energy (whose physical significance varies according to the adopted model) and C is a constant which is the ratio s/p , s being the probability of a non-radiative transition and p being the rate of emission of photons. Naturally if $s \gg p$ the phenomenon is most evident whereas if $s \ll p$ a appreciable thermal quenching does not occur.

If we suppose that the efficiency of the luminous transitions be somewhat dependent on temperature, the intensity of thermoluminescence would then be given by the product of (1) and (2).

Postulating that a phase transition gives rise to a variation of the coordinates of configuration, one can suppose some possible cases, assuming a variation of the force constant during phase transitions. In fig. 7 there are shown the configuration coordinates according to Hippel [15] and Mott and Seitz [16], of a luminescent center in which non-radiative transitions are very improbable (fig. 7 a). The activation energy E represents the energy necessary to take the system from lower vibrational levels of the excited state to levels whose energy is such as to permit non-radiative transitions from excited states to fundamental states. When a phase transition occurs (which implies an increase in the amplitude of vibration of the atoms and molecules

of the solid) the configuration coordinates may be widened (as is seen by the dotted curve in fig. 7 *a*). The configuration coordinates of the new phase would be more or less different from those of the initial phase (fig. 7 *b*) because of the different actions of the crystalline field on the luminescence centers [17]:

A) Let us consider the configuration coordinates of the type reported in fig. 7 *a*, in which the non-radiative transitions are only slightly probable (luminous center having a small Stokes shift). The widening of the configuration coordinate of the excited state (dotted line) is not large enough to intersect the configuration coordinate of the fundamental state: in this case the

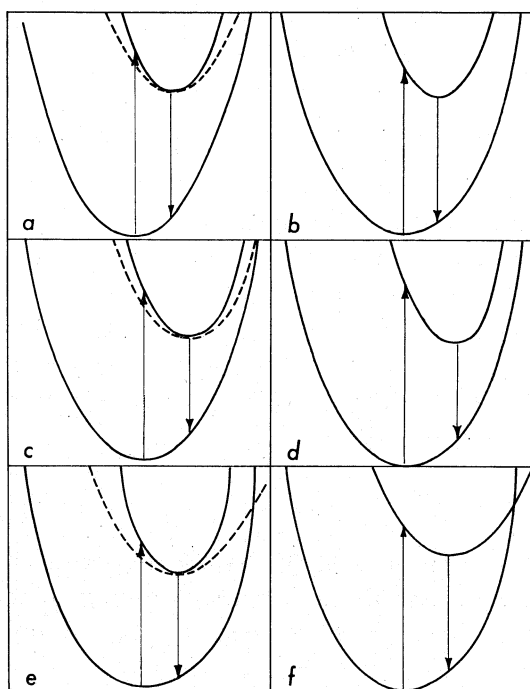


Fig. 7. – *a* and *b*: configurational coordinates in the case in which no characteristic variations are present at the phase transition temperature; *c* and *d*: case in which a small thermoluminescence minimum is present at the phase transition temperature; *e* and *f*: case in which a drastic breakdown is present, followed by a small luminous emission or no emission at all.

luminous efficiency is not varied during the phase transition in any appreciable way. Since the configuration coordinates of the luminescence center of the final phase are of the same type as those of the initial phase, the luminous efficiency does not vary even following the transition;

B) Let us examine the configuration coordinates whose excited state has only a slight probability of a non-radiative transition. During the phase transition, the configuration coordinate of the excited state can enlarge itself enough to be able to intersect the coordinate of the fundamental state (dotted curve – fig. 7 *c*): in such a case there occurs a brusque decrease in the effi-

ciency of the luminous process. If, in the final phase, the configuration coordinate of the excited state does not intersect that of the fundamental state (fig. 7 *d'*) then the efficiency of the process would return to its former elevated value. If this happens the intensity of thermoluminescence would return to its initial value (after the brusque decrease of the luminous efficiency);

C) Finally let us consider the case of a configuration coordinate whose excited state only a very small probability of a non-radiative transition. During the phase transition the coordinate of the excited state intersects the coordinate of the fundamental state (fig. 7 *e* – dotted line) followed by an abrupt decrease in the luminous intensity (as occurs in case B). But in the final phase if the coordinate of the excited state intersects the coordinate of the fundamental state (or is quite close) the luminous emission ceases (or reaches a very low value).

Among the compounds that were studied, case A was verified by phosphates of the type MeH_2PO_4 (fig. 6): there were no brusque variations noted at the corresponding phase transition temperature; Case B was verified by sulfur (rhombic-monoclinic transition) and by ammonium sulfate: the thermoluminescence curve of the latter substances showed a cusp-shaped minimum at the corresponding phase transition temperature. Case C is very evident in the three samples of $\text{H}_2\text{O}-\text{P}_2\text{O}_5$ system (glass-liquid transition) and in sulfur monoclinic-liquid transition): after the phase transition the luminous emission was very weak or completely absent.

CONCLUSIONS.

Relations between phase transition and thermoluminescence in some irradiated inorganic substances were looked into and the authors have presented three typical cases:

- A) phase transition not influencing luminous emission;
- B) phase transitions giving rise to cusp-shaped minima;
- C) phase transitions giving rise to a breakdown of luminous intensity.

These phenomena were explained keeping in mind the difference between the configurational coordinates of the initial phase and final phase and the variation of the vibrational amplitude of the atoms during the phase transition.

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