

TEMPERATURE VARIATION OF INTENSITY OF LUMINESCENCE UNDER X-RAY EXCITATION

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ABSTRACT. The variation of the intensity of X-ray luminescence with temperature ranging from 30°C to 150°C for sodium chloride, sodium chloride with copper, potassium chloride, potassium chloride with copper, potassium bromide, potassium bromide with copper, uranyl nitrate, naphthalene and anthracene has been obtained, the measuring instrument being a photocell with amplifying device. The variation curve is found to be of distinctly two types. The intensity of luminescence for sodium chloride, sodium chloride with copper, potassium chloride and the same with copper varies with temperature, at first slowly, then quickly, finally reaching almost a steady value in the temperature range under investigation. For potassium bromide and potassium bromide with copper, possibly only the later portion of the curve is obtained. For others the intensity of luminescence is almost temperature independent till the melting point is reached when intensity falls to zero. The inclusion of copper ions does not seem to make any qualitative difference in the behaviour of the phosphors.

It has been known for a long time that temperature is an important factor in determining the intensity of luminescence of a phosphor. Substances are known which fluoresce only at low temperature. An excited electron can release its energy and come back to its lowest state in two ways, either with emission of radiation or by dissipation of energy as heat. The variation of the relative probabilities of the two processes will obviously depend on the behaviour of the normal and excited states of the crystal with change of temperature. Various mechanisms have been suggested by Seitz (1930), Mott (1938) etc., to account for increase of probability of transference of excitation energy into heat with the rise of temperature.

At the present time the difficulties of directly determining the energy zones of even a simple crystal with sufficient accuracy are extremely great; in spite of the great deal of work done up to date, the mechanism of the production of luminescence with all its varied phenomena is as yet obscure. It is not unreasonable to expect that the investigations into the variation of intensity of luminescence with temperature may throw some light on the mechanism of luminescence, on the nature of the radiative centres etc. The temperature variation of the intensity of luminescence has, as yet, received very little attention from the experimental workers; the only work done is that of Randall (1937). He measured the intensity of luminescence at different temperatures (90°K - 600°K) for a number of sulphide phosphors. He has observed in general a drop in the intensity of luminescence with the rise of temperature. In certain phosphors, the intensity drops also at low temperatures; the cause of this drop is rather uncertain. Mott and Gurney (1940) have, however, tried to explain

it on the assumption that the incident light is of a wavelength which produces only excitations in the lattice. His results are shown in Fig. 1.

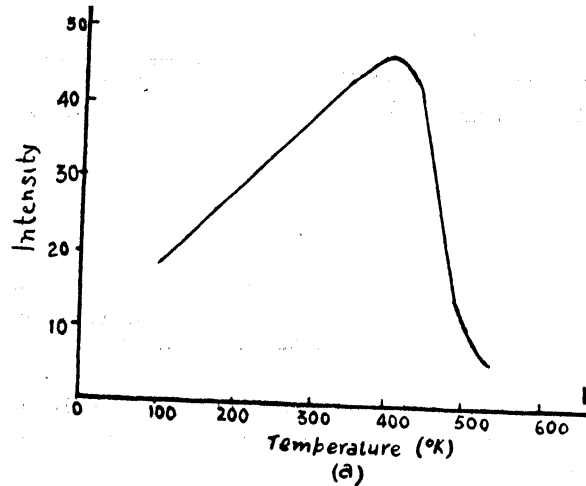


FIG. 1

Temperature variation of the intensity of fluorescent radiation in zinc sulphide phosphor.
(a) Impurities Mn, Mg, Ba, Si

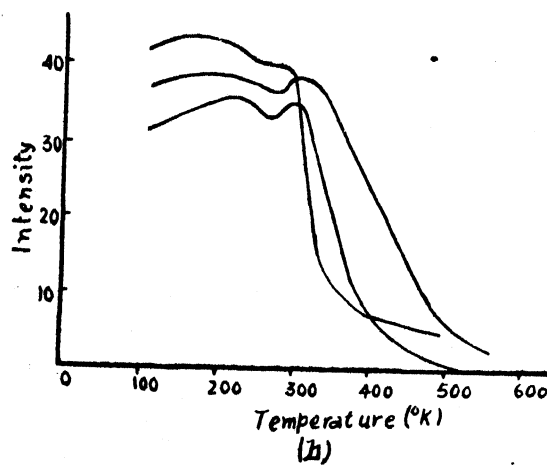


FIG. 1

(b) Various specimens activated by Ag, Cu, Mg

The present work differs from that of Randall in that the intensity of luminescence of different types of phosphors under X-ray excitation has been measured here while Randall measured the intensity of luminescence of phosphors like ZnS, ZnS + CdS etc., under ultraviolet excitation. As has been pointed out by Randall in ultraviolet excitation, the constancy of the absorption

temperature of the sample was measured with a calibrated thermo-couple placed in contact with the back side of the sample.

The measuring instruments* consisted of a photocell (type 868 R.C.A.) followed by a D. C. amplifier operating a milliammeter. The voltage applied to the photocell is adjustable and may be varied between 30 to 78 volts. The D. C. amplifier has been specially designed to have linear characteristics which did not sensibly change with use. The photocell possesses a dark current of about 1/100 of a micro ampere. Input resistances of 0.2 megohms, 2 megohms and 20 megohms are provided inside the meter to change the range of sensitiveness. A circuit diagram is shown in Fig. 2.

The measurements were also repeated with another photovoltaic cell connected directly to the galvanometer. As only relative values are required for the present purpose, readings of the meters have been plotted against temperature.

RESULTS AND DISCUSSIONS

Luminescence of sodium chloride and sodium chloride with copper impurity:

Temperature intensity curves are shown in figure 3. Samples of pure* chloride and copper activated sodium chloride were the same for which the lumi-

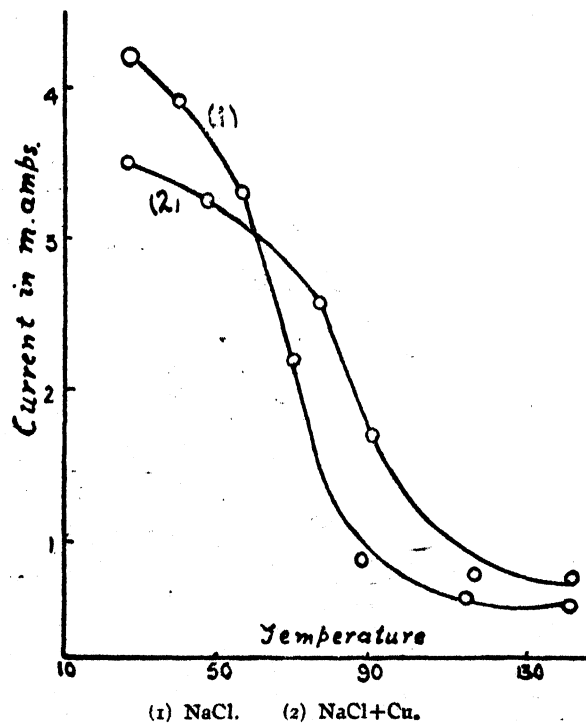


FIG. 3

* Foot candle meter was constructed and calibrated in the Wireless Laboratory of Physics, Calcutt University.

luminescence spectra have been photographed. A fall in the intensity with the rise of temperature is observed in both cases. The rate of decrease, at first small, quickly rises to a maximum and then falls again to almost zero value. The temperature at which the sharp decrease in intensity occurs is however different for the two samples. From the spectra of luminescence we find that the spectral region of emission does not appreciably change with the introduction of copper. However the intensity of luminescence decreases with the inclusion of copper ions as impurity. The temperature at which the steep fall in intensity occurs is also raised; the ratio of the limiting intensity of luminescence at high temperature to its intensity at 80°C is however greater for the impure sample.

Luminescence of potassium chloride and potassium chloride with copper impurity :

In this case also all experimental samples were prepared from the same material. The general nature of the results is the same as that found for sodium chloride. The inclusion of copper ions affects the total intensity of the phosphors, the temperature of maximum rate of change of intensity, and the residual intensity in the same way (Fig. 4).

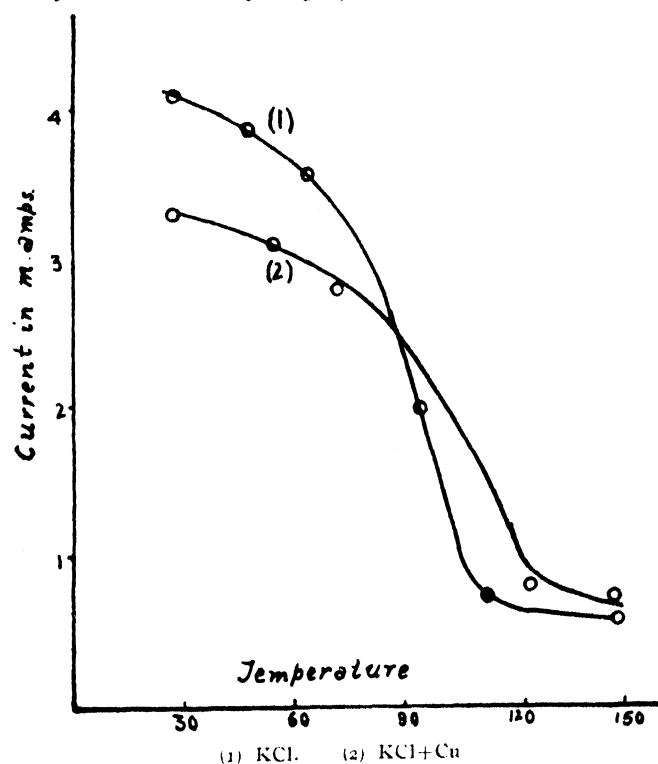
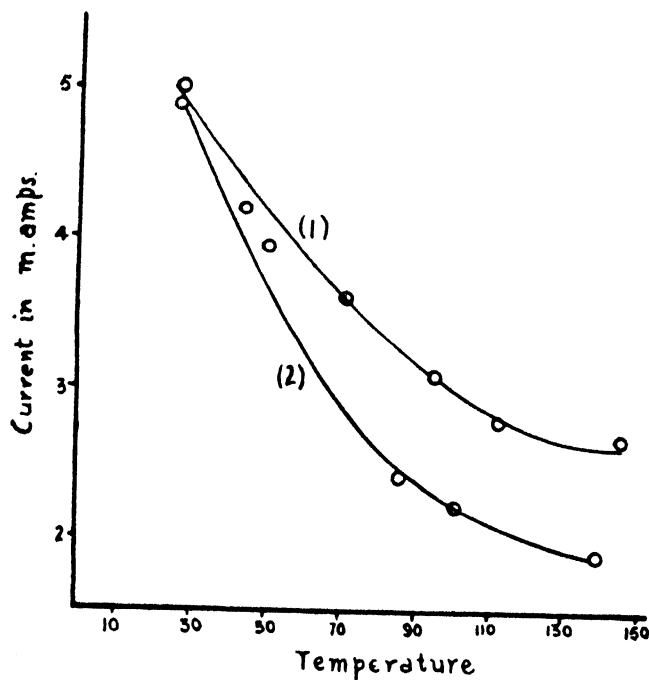


FIG. 4.

Luminescence of potassium bromide and potassium bromide with copper impurity :

In case of potassium bromide the intensity decreases gradually and no sudden decrease in intensity at a particular temperature is perceptible as in the

preceding two cases. The inclusion of copper ions does not also seem to produce any great change in the behaviour of the intensity of luminescence of the phosphors with change of temperature (Fig. 5).



(1) KBr+Cu (2) KBr

FIG. 5

Luminescence of uranyl nitrate :

The change of intensity of luminescence of uranyl nitrate with rise of temperature is shown in Fig. 6. The intensity of luminescence remains constant within experimental accuracy and suddenly falls to zero value at about 59°C. Uranyl nitrate used here was the hydrated variety containing six molecules of water of crystallisation. This hydrated uranyl nitrate melts, i.e., dissolves in its water of crystallisation, at about 59°C. The abrupt cessation of luminescence is therefore due to the breaking up of the lattice of the solid state.

Luminescence of naphthalene :

The temperature-intensity curve of naphthalene is shown in Fig. 7. The intensity of luminescence remains approximately constant up to about 80°C where naphthalene melts and ceases to show any perceptible luminescence.

Luminescence of anthracene :

Anthracene melts at about 216°C. The results of measurements above 150°C are not very accurate. The general nature of results appears to be the

same as that in the case of naphthalene or uranyl nitrate. The intensity of luminescence does not vary appreciably with temperature till the melting point is reached when the intensity suddenly drops to zero (Fig. 8).

All substances have been purified by repeated crystallisation before use; however it is quite possible that they nevertheless retained traces of unknown

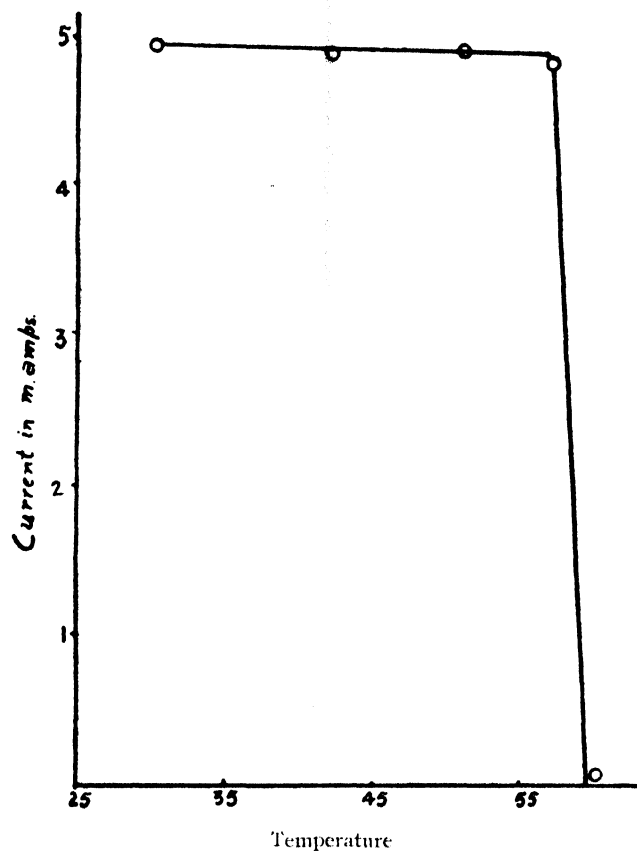


FIG. 6

impurities. Levy and West (1939) measured, by the spectroscopic method, the intensity of fluorescence and phosphorescence of zinc sulphide and found that it is greatly affected by minute traces of impurity. It is therefore difficult from the present measurement alone to come to a definite conclusion about the intensity of luminescence of the pure phosphors and the effect of inclusion of a particular impurity. In spite of this limitation it is however reasonable to think that the present investigation yields certain general results which are at least qualitatively correct.

The temperature variation of intensity of luminescence is found to be distinctly of two kinds. Crystals like naphthalene, anthracene and uranyl nitrate retain much of their molecular character in the solid state. The aromatic molecules like those of naphthalene and anthracene possess electrons which are

free to move round the molecule; possibly these are the electrons which are also responsible for the optical behaviour of crystals. In the case of uranyl nitrate the optical electrons of UO_2 group are responsible for the luminescence spectra; for, under ultraviolet excitation uranyl salts are found to fluoresce in the crystalline state as well as in solution; the fluorescence spectra in the two states are also identical except that the bands emitted in solution are more diffuse.

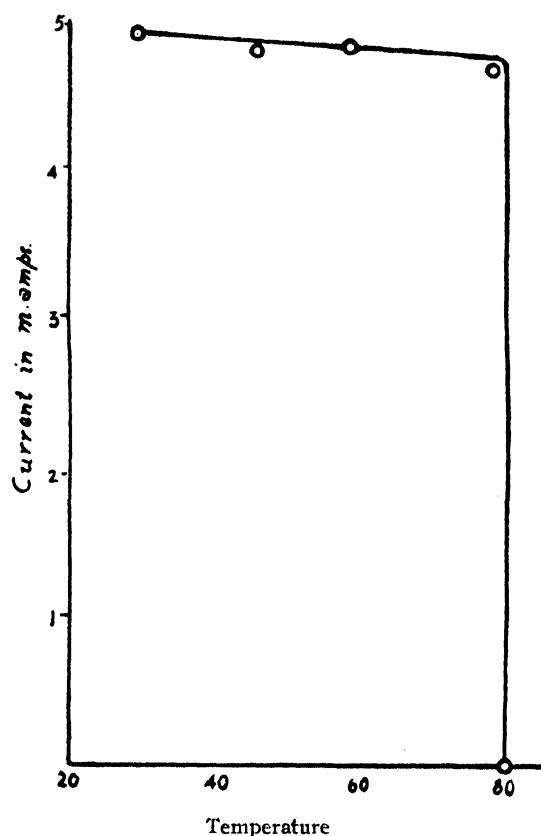


FIG. 7

In naphthalene, anthracene and uranyl nitrate, the optical electrons, though excited, do not leave the molecules or atomic groups to which they belong. In such crystals the intensity of luminescence is almost independent of temperature. There is thus an apparent connection between the rapid extinction and photo-ionisation of molecules.

Since the mass absorption coefficient of X-rays is independent of temperature, the number of photoelectrons produced per second within the crystal by the incident X-rays may be assumed to be constant. These electrons moving inside the lattice in all directions suffer collisions with the electrons and nuclei of the crystal and excite some of the optical electrons. The results of the present investigations show that the number of inelastic collisions suffered by the

photoelectrons with the molecules of a crystal is not much influenced by rise of temperature at least within the range of temperature under consideration.

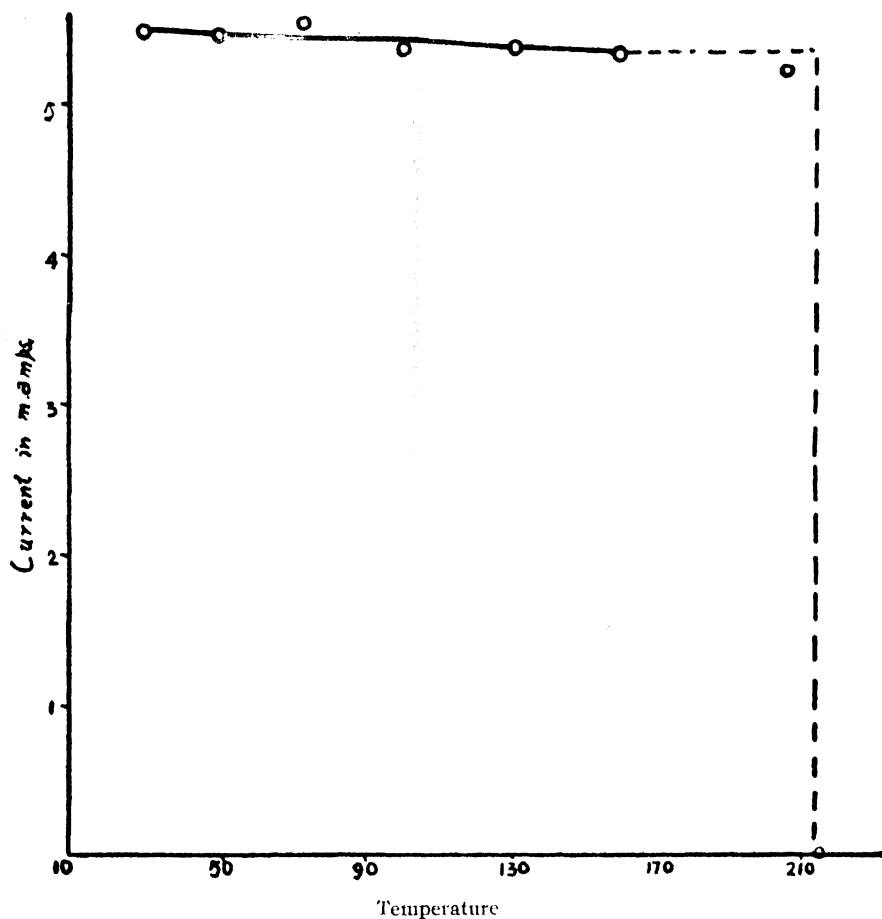


FIG. 8

The mechanism of luminescence of sodium chloride and potassium chloride crystals will be discussed in a separate paper (Luminescence of solids under X-rays). Without making any assumption as to the nature of the radiative centres we can assume that the number of centres where the electron can release its energy as radiation is not very large ; in general the released electron comes back to the valence band without emission, releasing its energy as heat ; otherwise the efficiency of luminescence would have been much larger. Even at those centres there is a probability that the non-radiative transitions should occur ; Peierls (1932) has considered the possibility of such transition. Though it is not yet possible to give quantitative data, he finds that the probability of non-radiative processes increases rapidly as the temperature is raised. In order to be able to interpret the curve in detail we need further knowledge about the radiative centres. If the centres be such as have been created by X-ray itself

(stoichiometric excess of sodium) then the rate of decrease of intensity of luminescence will be determined by the rate of production of such centres. Such centres created probably by the trapping of electrons will be brought back to their normal state by their release of thermal energy. In that case the sudden fall in intensity will occur at a temperature at which the trapped electron finds it most convenient to be rescued from the trap. The residual intensity may be due to the presence of a temperature independent mechanism for radiative transition even in these crystals. This is further justified by the presence of two bands in the spectra, one of them being rather sharp.

The behaviour of potassium bromide seems to be just intermediate between the two kinds of phosphors considered. It therefore appears that in potassium bromide two types of centres—one like that of uranyl nitrate and another similar to those in NaCl or KCl—are present; possibly only the later portion of the curve is obtained there.

The effect of inclusion of copper ions on the intensity of luminescence leads us to the conclusion that, unlike the thalium activated sodium chloride under ultraviolet excitation, in X-ray luminescence the impurity ions (at least the copper ions) are not directly responsible for the luminescence. The impurity influences the luminescence indirectly in this case; the intensity is decreased slightly, which is analogous to the quenching effect found in certain cases of ultraviolet excitation. In those cases the effect is explained as collision of second kind with the quencher whereby the energy is transferred without emission. In solids the mechanism cannot be the same; but it is possible that some of the excited electrons release their energy near the impurity centre without radiating.

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