

Effect of Pressure on Phosphor Decay*

D. W. GREGG AND H. G. DRICKAMER

Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois

An apparatus has been developed to measure the effect of pressure to over 50 000 atmospheres on the decay rate of phosphors. Three manganese activated phosphors with exponential decay curves were studied. In two cases the rate of decay decreased, in the third case it increased. A tentative explanation is offered. An hexagonal ZnS:Cu phosphor showed little pressure effect to 40 000 atmospheres at which pressure it transformed irreversibly to the cubic form with a sharp increase in decay rate and a large decrease in intensity.

AN apparatus has been developed to measure the effect of pressure on phosphor decay. It has been operated to 52 000 atmospheres, and, under favorable conditions, is capable of considerable extension of the pressure range. The high-pressure bomb and press is the same as that used for spectroscopic studies.^{1,2} The press is incorporated with a shutter system as shown in Fig. 1. The shutters are aluminum disks 13 in. in diameter cut as indicated in the figure, and rotated on a common shaft. A rubber wheel on the shaft makes a friction contact with a fly wheel turned by a 1/12 hp motor. The rpm can be adjusted by sliding the rubber wheel to different points on the radius of the fly wheel. The entire setup is enclosed to prevent light leak.

The light source is a BH-6 Mercury lamp which is focused on the bomb window with appropriate lenses. The phosphor output is focused on a 1P21 photomultiplier tube. The tube output goes to a Tektronix 122 Preamplifier, then to a Tektronix 545 Oscilloscope. The

decay curves were photographed with a Polaroid type 2620 camera. The transparencies were projected on a screen to permit more accurate measurement of the decay. Six to eight pictures were taken at each pressure, and each material was run with at least 2-3 separate loadings. In order to minimize shear effects, which are particularly serious with ZnS phosphors, the samples were suspended in Canada Balsam which was inserted in a hole drilled in the NaCl pressure transmitting "fluid."

RESULTS

Data were obtained on three manganese activated phosphors with substantially time independent exponential decays. These were Bureau of Standards numbers 1030, 1028, and 1025, which had compositions $(MgO)_x(As_2O_5)_y:Mn$, $ZnSiO_4:Mn$, and $Zn_3(PO_4)_2:Mn$. Plots of decay time versus pressure are shown in Fig. 2-4. In all cases the decays were reversible with pressure within the accuracy of the measurements. For phosphors 1030 and 1028 the decay constant increased by

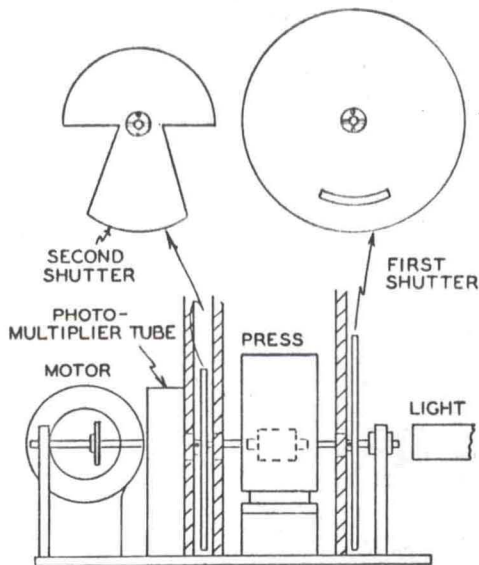


FIG. 1. Schematic diagram of high-pressure apparatus for decay studies.

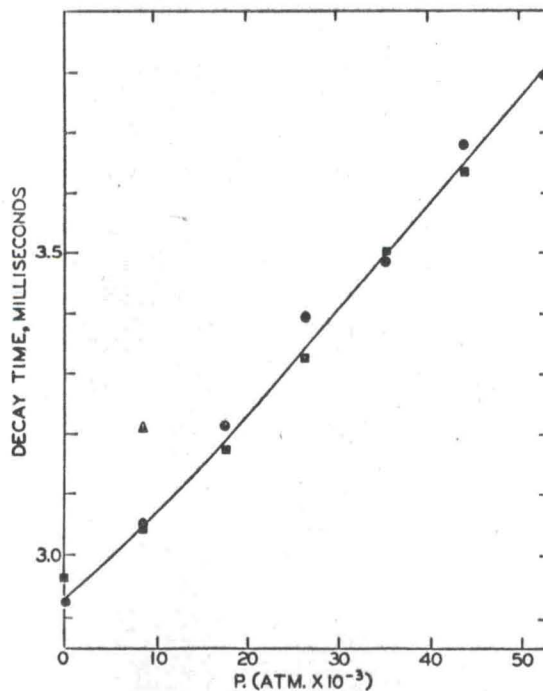


FIG. 2. Decay time vs pressure for $(MgO)_x(As_2O_5)_y:Mn$ (1030).

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¹ Fitch, Slykhouse, and Drickamer, J. Opt. Soc. Am. 47, 1015 (1957).
² T. E. Slykhouse and H. G. Drickamer, J. Phys. Chem. Solids 7, 210 (1958).

40–50% in 50 000 atmospheres (i.e., the rate of decay decreased). For 1025 (the $Zn_3(PO_4)_2$ phosphor) the decay constant decreased with pressure (i.e., the rate of decay increased).

A tentative possible explanation can be offered as is illustrated in Fig. 5. These constitute plots of energy *versus* a configuration coordinate for the ground and excited states similar to those of Leverenz.³ The configuration coordinate presumably is related to some characteristic dimension of the system. There are two factors which affect the location of the minimum in the excited state relative to that in the ground state. The higher energy tends to move the minimum to larger values of X (configuration coordinate). On the other

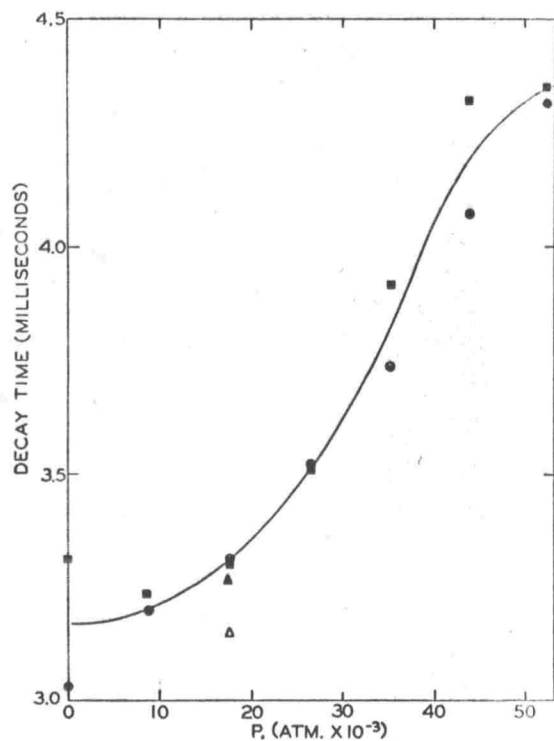


Fig. 3. Decay time *vs* pressure for $Zn_2SiO_4:Mn$ (1028).

hand, the fact that the manganese ion has at least partially lost an electron tends to bind the neighboring anions more tightly and move the minimum to smaller X . The minimum in the excited state may thus occur on either side of the ground-state minimum [Fig. 5(a) or 5(b)]. Let us assume (perhaps rashly) that the excited state always compresses more than the ground state. The rate of decay depends on the overlap between ψ_1 and ψ_2 . The decays are presumed to be vertical (Franck-Condon) processes. In case 5(a) where the excited state minimum occurs outside the ground state minimum, the effect of pressure in our picture will be

³ H. W. Leverenz, *Luminescence of Solids* (John Wiley & Sons, Inc. New York, 1950).

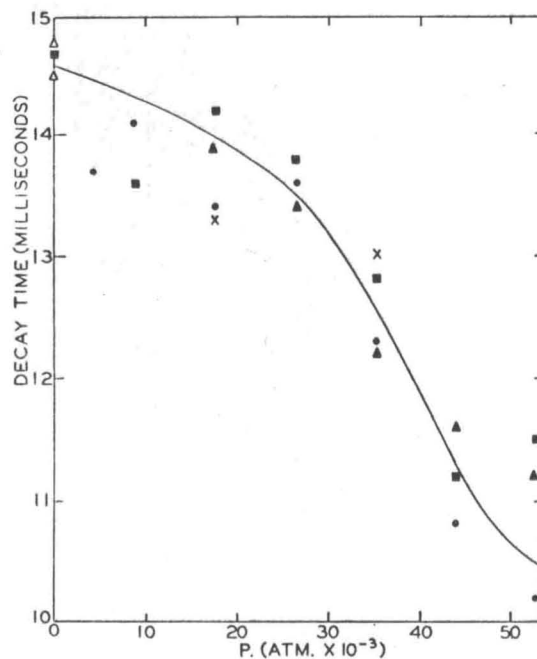


Fig. 4. Decay time *vs* pressure for $Zn_3(PO_4)_2:Mn$ (1025).

to increase the overlap and decrease the decay constant, i.e., to cause the phosphor to decay faster. This is so because the ground-state level ψ_1 to which the phosphor decays is more concentrated at high pressure. In case 5(b) where the excited state minimum occurs inside the ground-state minimum, the opposite effect would obtain. This explanation is purely speculative, but worthy of consideration.

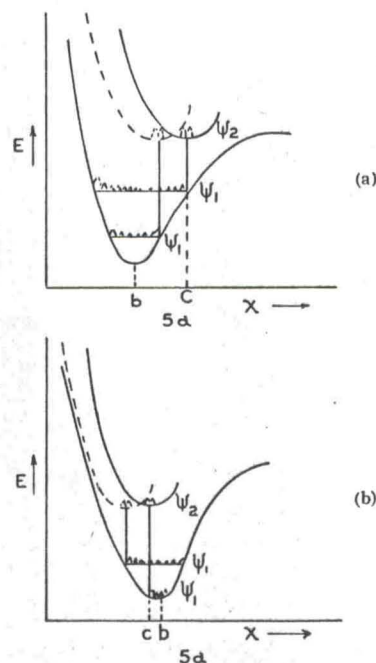


Fig. 5. Energy *vs* interionic distance: Mn^{++} in solid phosphor.

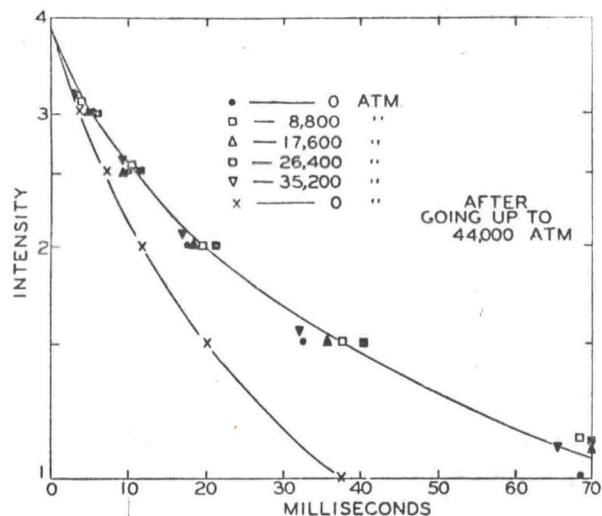


FIG. 6. Intensity vs pressure ZnS:Cu (1020).

Some measurements were also made on an hexagonal ZnS:Cu phosphor (BS No. 1022). Since the decay is

not a simple exponential, no characteristic time can be given, but decay curves are shown in Fig. 6. The rate of decay was substantially independent of pressure to 35 000 atmospheres. In the neighborhood of 40 000 atmospheres there was an apparent abrupt increase in the decay rate accompanied by a large decrease in intensity. The rate at high pressure was difficult to reproduce because of low intensity. This change of decay rate was irreversible, as the rate changed only slightly upon returning to one atmospheric pressure. X-ray powder patterns of the material before and after pressurizing showed that the hexagonal crystal had been converted substantially completely to the cubic (zincblende form). A pressure induced transition of this kind would be expected as the stable low-temperature form is cubic. Some measurements were attempted on another cubic ZnS:Cu sample, but intensities were too low for good data. There seemed to be a measurable increase in decay rate with pressure.