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Pressure Effects in Luminescence: Isobaric Experiments on NaI(Tl)†

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The effect of steady-state hydrostatic pressure on the properties of luminescent systems, with particular reference to the phosphorescence of NaI(Tl), is examined. It is shown that readily observable changes in decay mean life may be produced by very modest pressures. An interpretation of these effect is developed from a configurational coordinate model and also from thermodynamic considerations. Experimental results are in good agreement with these theoretical expectations. For a 0.66-ev trap in NaI(Tl), the change in center volume at the point of transition from metastable to emitting state is found to be $+17.5\times10^{-24}$ cm^3. Assuming a specific model for the center allows computation of the sign and magnitude of the critical displacement of ions required for trap collapse—in this case +0.19 A. The force constant for the metastable state is computed to be 5.8×10^5 dynes/cm; and the vibrational frequency, assuming an effective mass equal to six I^- ions, is 3.4×10^{12} sec^{-1} corresponding to a zero point energy for this trap of 0.007 ev and cross over at a vibrational quantum number of about 47. The transmission coefficient for cross-over to the emitting state appears to be of the order of 0.03%. Other possible experiments involving steady-state or transient pressure effects are outlined.

I. INTRODUCTION

LUMINESCENCE in the solid state has been studied extensively using temperature as an independent variable. In addition to measurements on emission and absorption spectra, methods employing thermoluminescence or "glow curves," or isothermal decay over a wide range of temperatures have been highly refined and applied to a variety of luminescent systems. The present work is part of a program explicitly concerned with examining the utility of pressure as well as temperature as an independent variable in luminescence studies. With the exception of a few experiments concerned with pressure effects on absorption spectra, no systematic examination of this possibility appears to have been made. For reasons sketched previously,[1] we have chosen first to explore the effect of pressure on the long-term phosphorescence of thallium-activated alkali halides excited by a pulse of gamma radiation.

Detailed study of the kinetics of deep traps in the phosphor NaI(Tl) have been made by Emigh and Megill.[2] Furthermore, it has been established from the qualitative measurements reported in I that as little as 2000 psi will produce observable effects in NaI(Tl). In I, no attempt was made to construct a detailed and quantitative explanation of the results because of the complex nature of the decay resulting from the presence of many different electron trapping levels in the material. If one assumes, however, that the phosphorescent decay is the sum of a number of independent first order processes as suggested by the analysis of Emigh and Megill, then the pressure-sensitive behavior of individual traps in the phosphor may be isolated. In fact, a reasonable interpretation can be given without detailed knowledge of the kinetics provided only that escape from traps is the rate determining step in the sequence. If monomolecular kinetics are assumed and if traps are identified with Tl^+ ions substitutionally imbedded at cation sites in the lattice, one may calculate a critical displacement in the configuration coordinate required for thermal ionization or collapse of a trap.[3]

An interesting aspect of pressure effect experiments is that they permit differentiation of phenomena resulting from asymmetries with respect to equilibrium positions. Put differently, external pressures applied to a phosphor system exert forces which are always directed so as to make interionic spacings decrease—to make certain of the important configurational coordinate values smaller. This may be contrasted with experiments involving temperature effects (e.g., thermoluminescence) in which the excursion of the system over both larger and smaller values of the coordinates is modified. It follows that the pressure sensitivity of phosphorescence allows the location of "cross-overs" between configurational potential curves for metastable and emitting states, a problem which does not yield readily to more conventional approaches. In particular, the sign of the displacement required for thermal ionization or collapse of a trap may be determined. That this is possible, of course, follows as a direct consequence of Le Chatilier's principle.

II. THEORETICAL CONSIDERATIONS

The general configuration coordinate diagram for a trapping site is shown in Fig. 1. We assume the excitation energy is stored in the form of an electron localized at an activator or other defect in the lattice. As one

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[1] L. Reiffel, Phys. Rev. 94, 856 (1954), hereinafter referred to as I.

[2] C. R. Emigh and L. R. Megill, Phys. Rev. 93, 1190 (1954).

[3] L. Reiffel, Proceedings of the International Conference on Solid-State Physics in Electronics and Telecommunications, Brussels, June, 1958 (to be published). The slightly different numerical values reported in the present paper result from improvements in correction of the raw data and more detailed study of temperature dependence.

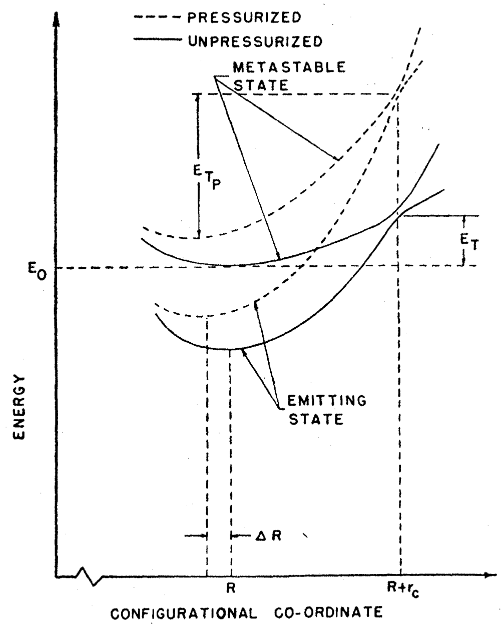

FIG. 1. Configurational coordinate diagram for phosphorescent center. The relative energies of the metastable and emitting states are not significant and the effect of pressurization is greatly exaggerated for clarity.

possibility leading to phosphorescence, thermal collapse may occur with the system passing from a metastable state into another state associated with the same defect from which an allowed optical transition may take place. As a second possibility, thermal ionization may occur perhaps followed by an optical transition in an interaction remote from the trapping site. Retrapping may be possible in either situation although it is traditionally considered only in the case of thermal ionization. Even in transitions not involving the conduction band, one metastable state might feed another in the same center, especially in relatively complex centers. We assume that at crossover an energy E_T is required either for thermal ionization or for collapse and that the system may be represented by a parabolic potential. The equilibrium value of the coordinate is R while the additional energy E_T places the system in a vibrational state ranging out to $R\pm r_c$. Thus r_c is the critical increase (or decrease) in configurational coordinate required for emptying of the trap. Also shown in Fig. 1 are curves for an emitting state to illustrate the usual close approach of the two potentials at E_T.

If a hydrostatic stress is now applied to the system, the potential energy surfaces for the system will be altered from the solid curves of Fig. 1 to the dotted curves—obtained by assuming that a linearly increasing potential ascribable to the applied stress may be added to the potential resulting from the normal forces acting on the center. Evidently, the additional potential energy is a function only of position in this model and is the same for all states of excitation at fixed position. Thus, the energy of transition is independent of the pressure, but there is a change in energy separation between a potential minimum and the potential at a given distance from the equilibrium configuration. This change, due to the pressure, is an increase if the point in question is to the right of the minimum and a decrease if the point is to the left of the minimum. If a given location in configuration space must be attained before the system can go from the metastable to the emitting state then the change in energy separation is precisely the change in trap depth for the process.

Let E_m be the potential energy for a given configuration of the activator ion and its ligands when the activator is in its metastable state, E_0 the energy minimum of the metastable state, E_T the energy of the "cross-over" between metastable and emitting state under no pressure and with reference to the normal minimum for the metastable state, R_0 the spacing between the activator and its ligands at equilibrium in the metastable state, and r_c the displacement from equilibrium at which the crossover energy E_T is achieved. We may define a force constant C_m (assumed independent of pressure) for the metastable state from which

$$E_m(r)=\tfrac{1}{2}C_m(r-R_0)^2+E_0,$$

and

$$E_T=\tfrac{1}{2}C_m(r_c)^2. \tag{1}$$

Under pressurized conditions

$$E_m(r)=\tfrac{1}{2}C_m(r-R_0)^2+E_0+\alpha pr, \tag{2}$$

where α is an effective area which may, under certain conditions, be identified with the projected area of the ligands acting on the activator; p is the applied hydrostatic pressure. From (2), by differentiation,

$$R_p=R_0-\alpha p/C_m.$$

The energy at equilibrium under pressure is given by

$$E_m(R_p)=\tfrac{1}{2}C_m\left(-\frac{\alpha p}{C_m}\right)^2+E_0-\frac{\alpha^2p^2}{C_m}+\alpha pR_0,$$

while the energy for thermal collapse is

$$E_m(R_0+r_c)=\tfrac{1}{2}C_mr_c^2+E_0+\alpha pR_0+\alpha pr_c.$$

The trap depth, under pressure, is

$$E_{T_p}=E_m(R_0+r_c)-E_m(R_p),$$

from which

$$E_{T_p}=E_{T0}+\alpha pr_c+\tfrac{1}{2}\frac{\alpha^2p^2}{C_m},$$

or

$$E_{T_p}=E_T\left[1+\frac{\alpha pr_c}{E_T}+\tfrac{1}{4}\left(\frac{\alpha pr_c}{E_T}\right)^2\right]. \tag{3}$$

Under circumstances such that $\alpha pr_c\ll E_T$, that is for deep traps or for modest pressures, the change in trap depth due to pressurization is simply $\Delta E=\alpha pr_c$ since the quadratic term may be ignored. These results should apply for pressures at which α and C_m are not seriously altered.

If monomolecular kinetics are assumed, the phosphorescent light level as a function of time with pressure as a parameter may be expressed as

$$B(t,p)=\sum_i N_i \frac{1}{L_i(p)} \exp\left(\frac{-t}{L_i(p)}\right), \qquad (4)$$

where N_i is the filled population of the ith trap at $t=0$, $L_i(p)=A_i^{-1}(p)e^{E_i(p)/kT}$ = mean life of trap, $A_i(p)$ is the frequency factor for the ith trap, and $E_i(p)$ is given by Eq. (3); r_c and α are not necessarily the same for different traps.

It seems reasonable, in view of the small distortions of the configurational coordinate diagram involved, to assume that the $A_i(p)$ terms are not strongly affected by the pressures attained experimentally; these terms will hereafter be considered constants. It is also likely that trapping cross sections will not depend markedly on pressure in our working range so the relative populations will depend only on excitation conditions and time. This clearly becomes a more critical assumption when re-trapping processes are important in determining the behavior of the phosphor. Equation (4) may be simplified markedly for the situation when one trap is dominating the decay, in which case

$$B(t,p)=[N_0/L(p)]e^{-t/L(p)},$$

and the ratio of mean lives for pressurized and unpressurized conditions becomes

$$L(p)/L(0)=e^{\alpha p r_c/kT}. \qquad (5)$$

This ratio may be obtained from experiment in at least three ways: (1) Determine mean lives from constant pressure isothermal decay using graphical peel-off methods.[2] (2) Select experimental conditions such that only one trap is important and obtain constant pressure isothermal mean life data. (3) With conditions as in (2) make step function pressure changes and obtain resulting intensity variations. For fast changes in p, the trap populations can be considered constant and

$$L(p)/L(0)=B(0)/B(p).$$

Equation (5) was derived on the basis of a two-dimensional configurational coordinate model for what is in fact a multidimensional problem. If synchronous radial oscillation of the Tl$^+$ ligands is the dominant mode, this simplification is readily justified. Elaborating on suggestions by Seitz,[4] Williams[5] has presented arguments from which he concludes that this mode is indeed dominant for the prompt fluorescence of KCl(Tl) and involves the $^1S_0$, $^3P_1{}^\circ$ and $^1P_1{}^\circ$ states of isolated Tl$^+$ ions in the lattice. Patterson and Klick[6] have recently re-examined the emission and excitation spectra of KCl(Tl) and conclude that the state assignments proposed by Johnson and Williams may not be correct. In particular, they question the idea that the 4750 A emission band is due to the $^1P_1$ to $^1S_0$ transition while the 3050 A emission is from the $^3P_1$ to $^1S_0$ transition in the same Tl center. They suggest that these two emissions may originate in different centers and that the temperature dependent intensity ratio for the two bands, explained on the basis of thermodynamic equilibrium between $^3P_1$ and $^1P_1$ by Johnson and Williams, may be actually the result of other effects such as quenching in the 4750 A center.

Seitz attributed long-lived phosphorescence in the thallium-activated alkali halides to the presence of Tl$^+$ ions in adjacent cation positions in the lattice. The argument is based on absorption measurements by Bünger and Flechsig[7] who showed that ultraviolet absorption leading to phosphorescence varied as the square of the Tl content. Clearly, the properties of associated Tl$^+$ ions acting as one center cannot be fully described by a single variable related to the radial displacement of surrounding anions. Such a center has cylindrical symmetry and involves ten nearest and nonequivalent I$^-$ ions in the case of NaI. There are, in fact, three different classes of nearest anion neighbors for such a center. For a decrease in the Tl$^+$-Tl$^+$ separation, such as might be produced by homopolar bonding in the excited state,[8] two of these groups move inward, but the third could even move outward on the basis of a simple hard-sphere model.

In view of these complications, one would generally be forced to treat the model of Fig. 1 without explicit identification with physical displacements. It is thus important to observe that the equivalent of Eq. (5) can be derived from purely thermodynamic considerations by applying results developed for chemical reactions in dilute liquid solutions by Evans and Polanyi.[9] If K is the rate constant for a reaction, they show that

$$-kT(\partial \ln K/\partial p)=\Delta V^+, \qquad (6)$$

where ΔV^+ is the increase in volume accompanying the formation of the transition state.[10] We may identify the attainment of the crossover energy at r_c in the configurational coordinate model of Fig. 1 with this transi-

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[4] F. Seitz, J. Chem. Phys. **6**, 150 (1938).

[5] F. Williams, J. Chem. Phys. **19**, 457 (1951). See also P. D. Johnson and F. E. Williams, J. Chem. Phys. **20**, 124 (1952). For criticisms and comments on the Williams model specifically concerned with oscillator strength predictions, see R. S. Knox and D. L. Dexter, Phys. Rev. **104**, 1245 (1956); and Williams, Segall, and Johnson, Phys. Rev. **108**, 46 (1957).

[6] D. A. Patterson and C. C. Klick, Phys. Rev. **105**, 401 (1957).

[7] W. Bünger and W. Flechsig, Z. Physik **67**, 42 (1931); and **69**, 637 (1932).

[8] Reference 4, p. 160.

[9] M. G. Evans and M. Polanyi, Trans. Faraday Soc. **31**, 875 (1935).

[10] Glasstone, Laidler, and Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, New York, 1941), p. 11. Also H. Eyring, J. Chem. Phys. **3**, 107 (1935); W. F. K. Wynne-Jones and H. Eyring, J. Chem. Phys. **3**, 492 (1935).

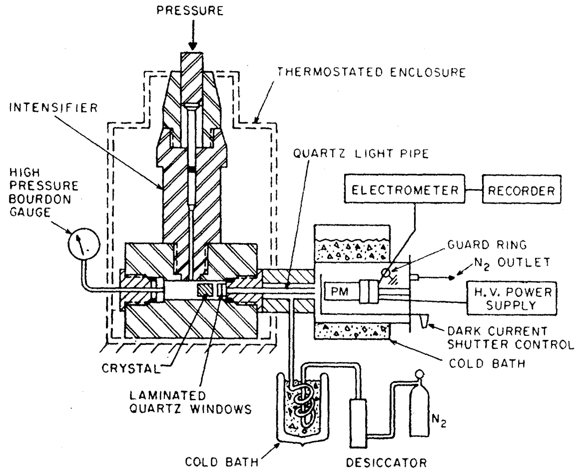

FIG. 2. Schematic diagram of experimental arrangement. High-pressure volume is equipped with additional window and thermocouple plugs, not shown.

tion state. ΔV^+ is then the net change in volume of the center and its surroundings at crossover and can be the result of shifts in many of the coordinates of the center. If these shifts are not very pressure-sensitive, we may immediately integrate Eq. (6) to obtain Eq. (5) with ΔV^+ replacing (αr_c). The assumption that ΔV^+ is not a strong function of p, thereby allowing direct integration of Eq. (6), is, of course, equivalent to neglecting the quadratic term in Eq. (3) since this arises from the shift ΔR in the potential minimum of Fig. 1 with pressure. Note that ΔV^+ is essentially an atomic property while p is easily defined only if the active center is treated as though it were imbedded in a continuum. Such a continuum model applied to a Tl^+-Tl^+ center would still yield a term approximately of the form $\Delta V^+ = (\alpha \bar{r}_c)$ where α is the effective area of the I^- nearest neighbors and $\bar{r}_c$ is an average radial displacement of these neighbors.

A more detailed study of the phosphorescence of KCl(Tl) by Johnson and Williams[11] makes a categorical assignment of the origin of long-lived phosphorescence to Tl^+-Tl^+ centers improbable. They find that certain thermoluminescence peaks in the range 200°K to 325°K show a concentration dependence appropriate to isolated Tl^+ ions, while a broad peak at 250°K behaves like a Tl^+-Tl^+ trap. For the most prominent of the former, they give a thermal depth of 0.72 ev and a frequency factor of about 10^8 sec^{-1}. Inspection of their curves shows that these isolated Tl^+ traps will be particularly important for long excitation times (such as used in the present experiments) and should dominate the later portions of the room temperature decay. Parenthetically, it may be noted that Johnson and Williams identify the two major traps in KCl(Tl) with the $^3P_2{}^\circ$ and $^3P_0{}^\circ$ states of isolated Tl^+. The validity of this identification does not affect the present discussion.

One concludes, therefore, that Eq. (5) should adequately describe the behavior of the phosphorescence of the thallium-activated alkali halides as a function of pressure for our experimental conditions. If Tl^+-Tl^+ centers are involved, only the product $\alpha \bar{r}_c = \Delta V^+$ has a simple interpretation. However, if the behavior of NaI(Tl) parallels that of KCl(Tl), then isolated Tl^+ centers are probably most important. In this case, the centers are symmetrical, all anions are equivalent, and a single coordinate r_c might well describe the situation satisfactorily.

III. EXPERIMENTAL CONSIDERATIONS

A schematic cross section of the pressure vessel for low level light measurements, showing the method of optical coupling from crystal to photomultiplier, is given in Fig. 2. There are, in reality, two windows on diametrically opposite sides of the pressurized volume. Each of the windows consists of two bonded fused quartz disks 0.700 in. in diameter and 0.250 in. thick. One window is coupled to a six-inch long 0.25-in. diameter polished quartz light pipe leading to the photomultiplier (PM). The light pipe is supported on knife edges inside the window retaining plug which is designed to provide an unsupported and unobstructed window aperture of 0.2-in. diameter. A short gap is left between the light pipe and the PM photocathode to allow insertion of a mechanical shutter for reading dark current. The second window is used for transmission measurements and is also convenient for checking the system response to external light sources with known properties.

Since it is desirable to follow the phosphorescence for long times and since the optical losses through the system are quite large, it becomes necessary to work with very low light levels. The PM tube is, therefore, equipped with a special guard ring geometry immediately surrounding the glass-to-metal seal for the anode lead to reduce socket leakage. To reduce dark current, the PM photocathode is cooled by immersing the tube housing in a cold bath and blowing cold, predried nitrogen through the housing and over the socket connections. The latter helps measurably in maintaining long-term stability against variations in leakage. Anode current in the range 10^{-7} to 10^{-13} ampere is measured with an electrometer circuit driving a standard recording milliammeter.

The crystal is immersed in a pressure-transmitting medium of good optical quality, usually mineral oil, and the system is pressurized through an intensifier using a small accumulator and an automatic pump. The pump is controlled by sensing the low-pressure side of the pressurizing piston, but data on the actual pressure are obtained with a carefully calibrated high-

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[11] P. D. Johnson and F. E. Williams, J. Chem. Phys. 21, 125 (1953).

pressure gauge connected directly to the experimental volume.

It is clear from the form of Eq. (5) that good temperature stability is required at the crystal. The entire pressure bomb is, therefore, enclosed in an insulated case lined with heating elements and cooling coils. Temperature is controlled using a series of preset thermal switches and checked with a precision thermometer in a small well in the body of the bomb. Long-term temperature control to an accuracy of approximately 0.1°C is usually achieved.

The system is designed to permit measurements from about +50°C to −20°C so the PM tube and associated components, which operate at about −80°C, are carefully insulated from the rest of the system.

Excitation of the crystal is accomplished with an external source of gamma radiation which is inserted into a hole in the bomb wall penetrating to within 0.5 in. of the crystal. The source hole is lined with a Hevimet tungsten alloy collimator. Early experiments were done with a 0.1-curie Co^{60} source emitting 1.24-Mev average energy gammas, but irradiation of the quartz windows produced large amounts of interfering phosphorescence. Changing to a 1-curie iridium-192 source emitting a complex gamma spectrum from 0.14 to 0.65 Mev allowed much better collimation within the available space and reduced scattering so the window luminescence was tolerable. Excitation is generally for a 10-minute period after which the decay is followed for several hours.

The experimental apparatus was subjected to a number of tests to establish reliability of the data, including checks on the linearity and stability of electronics and recording system and the linearity and hysteresis of the optical system. The latter was determined using an external light source and a series of neutral density filters. Even though one is dealing with data taken in the time domain under isothermal and isobaric conditions, it is important to establish the insensitivity of the system to changes in spectral distribution at all pressure levels. It is well known that traps of different depth may lead to emission at different wavelengths. Differential filter studies on NaI(Tl) indicate some spectral shift as the long-lived traps (∼1 ev) begin to dominate the decay. This shift is to longer wavelengths. If the optics exhibited a pressure-sensitive spectral dependence, such an effect would distort the time dependence of the phosphorescence at various pressures and temperatures by weighting traps differently. An external light source equipped with filters to isolate various wavelength bands was used to establish that these effects were small. Other pressure-induced changes, such as the gross lens effect produced in the optical windows, refractive index changes, alterations in spectral output or trapped light, are not important for these experiments. They are significant in transient-pressure studies and for other forms of excitation.

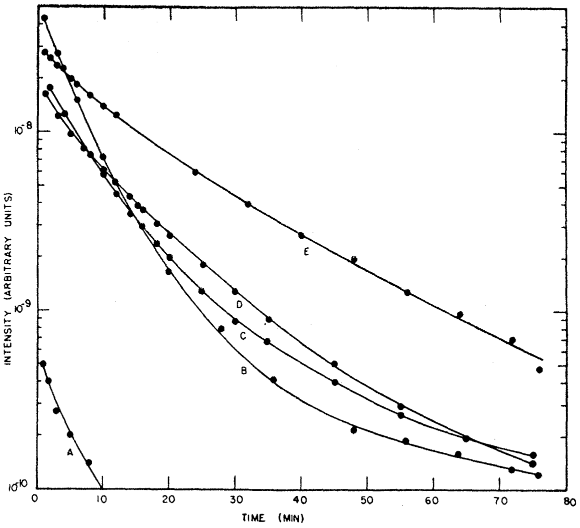

FIG. 3. Phosphorescent decay curves for NaI(Tl) at various pressures and 15°C. Thallium concentration 0.109 weight percent. Curve *A*: window phosphorescence only—all other curves have been corrected for this effect; Curve *B*: atmospheric pressure; Curve *C*: 15 000 psi; Curve *D*: 25 000 psi; Curve *E*: 40 000 psi.

IV. RESULTS

All results to be presented are for NaI(Tl) containing 0.109 weight percent Tl in the crystal. Typical phosphorescent decay curves for crystals subjected to various constant pressures during both irradiation and decay are shown in Fig. 3. Peel-off procedures applied to curves such as these can be used to isolate the behavior of traps with appropriate lifetimes. Under the experimental conditions prevailing, the trap for which this procedure is most reliable exhibits a thermal depth of 0.66±0.05 electron volt as determined from analysis of a series of isothermal phosphorescent decay curves at atmospheric pressure. Figure 4 gives mean life data at atmospheric pressure *vs* $1/T$ for the isolated 0.66-ev trap on which this trap depth value is based. Table I lists mean lives at a variety of temperatures and pressures for isolated traps. The trap at 0.98±0.1 ev could be determined reasonably well from the data, but the pressure effect lengthened the mean life and thereby reduced the light intensity to the point where accurate results could not be obtained by these steady state methods except at the highest temperatures. Most of the results therefore concern the 0.66-ev trap although qualitatively similar behavior is observed for the 0.98-ev trap.

The presence of both deeper and shallower traps has been detected but no attempt has been made to examine their behavior as a function of pressure. The two traps whose depth can be specified agree, within experimental error, with traps *B* or *C* and *D* of the Emigh and Megill analysis. A frequency factor assignment of 1.0×10^9 sec^{-1}, obtained for our 0.66-ev trap on the basis of Fig. 4, corresponds reasonably well to results on their

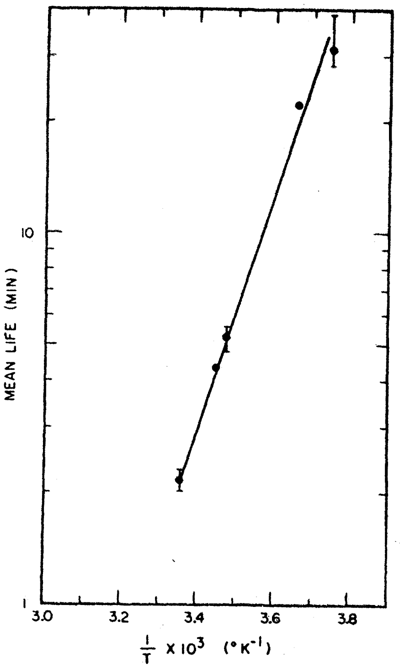

FIG. 4. Mean life *vs* temperature for isolated 0.66-ev trap in NaI(Tl).

trap *B*. Similar data for thallium in a KI host have been obtained by Smaller and Avery[12] who give a depth of 0.65 ev and a frequency factor of 1×10^{10} sec^{-1} for what may well be the same trapping state. For substitutional Tl, the nearest neighbors are iodine ions in both cases. Order of magnitude agreement in the frequency factor among the various determinations is all one may expect in view of the overriding influence of very small errors in the trap depth value.

In Fig. 5, the logarithm of the ratio of mean life under pressure to mean life at one atmosphere has been plotted as a function of pressure for the 0.66-ev trap. The linear behavior is precisely that predicted by the analysis leading to Eq. (5). These results allow a determination of the sign of ΔV^+ and, within the limits discussed previously, they provide a value of r_c. In turn, this permits calculation of other properties of the metastable center. It is of interest that these results rest upon measurements involving trap depth changes and not upon absolute values. The absolute magnitude of the change, at the pressures employed, is of the order of 10 millivolts and is known to an accuracy of perhaps two millivolts, whereas the depth itself can be measured only to an accuracy of 50 or 100 millivolts.

From Fig. 5 one obtains for the 0.66-ev trap $\Delta V^+ = +17.5$ A^3. Trap collapse thus occurs for a net increase in site volume corresponding to an outward displacement. The configurational coordinate schematic given by Emigh and Megill must therefore be revised if it is to be applied to this trap since it would predict a negative ΔV^+.

If a value of $\alpha = 93$ A^2 is assumed, corresponding to the projected area of six I$^-$ ions with Goldschmidt radii of 2.2 A, one obtains $\bar{r}_c = 0.19$ A.

If the harmonic oscillator-symmetrical mode is dominant, this value of r_c together with the trap depth value can be used to calculate the force constant for the metastable state using Eq. (1), yielding $C_m = 5.8\times 10^5$ dynes/cm.

Knowing C_m, one can find the vibrational frequency of the system if the effective mass is known. For the radial mode calculation in KCl(Tl), Williams[13] has found $M_{\text{eff}} = 6M_{\text{Cl}} + 6\beta^2 M_K$, where β is a coupling constant computed to be 0.4 on the basis of lattice relaxation to minimum energy. If this is used for a crude estimate in NaI, one obtains an effective mass less than 4% greater than that of the nearest I$^-$ ions alone. Since the Na$^+$ ions are light compared to the I$^-$ ions, a large error in β will not make a serious change in M_{eff} so we may compute the vibrational frequency with $M_{\text{eff}} = 6M_{\text{I}^-}$ and obtain $f = 3.4\times 10^{12}$ sec^{-1}. It should be noted that this corresponds to a zero-point energy of the system of 0.007 ev, implying that trap collapse occurs for a vibrational quantum number of about 47. This is comfortably high and means that a completely

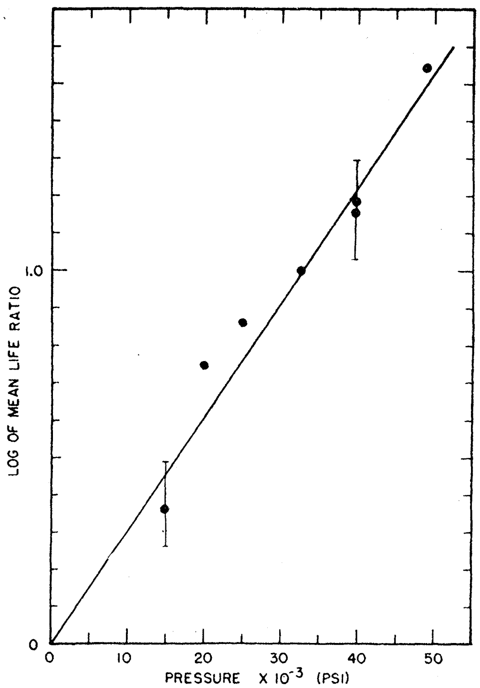

FIG. 5. Plot of log(mean life ratio) as a function of pressure for isolated 0.66-ev trap in NaI(Tl). The straight line is the theoretical fit to the data using Eq. (5) with $(\alpha r) = +17.5\times 10^{-24}$ cm^3. The indicated accuracy is estimated from the probable errors in assigning mean lives from the raw decay curves.

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[12] B. Smaller and E. Avery, Phys. Rev. **85**, 766(A) (1952).

[13] F. E. Williams, Phys. Rev. **82**, 282 (1951).

TABLE I. Compilation of mean lives for isolated traps in NaI(Tl) for various pressures and temperatures.[a]

	Trap one										
Temp. (°C)	15	15	15	15	17	17	17	17	17	24.8	24.8
Press. (psi)	AP	15K	25K	40K	AP	20K	32.5K	40K	49K	AP	40K
Mean life (min)	5.2±0.4	7.5	11.8	17.3±2.9	4.3	9.1	11.9	14.1	20.4	2.2±0.1	5.8
	Trap two										
Temp. (°C)	15	15	15	24.8	24.8						
Press. (psi)	AP	15K	25K	AP	40						
Mean life (min)	46.2±5.8	>38	>35	18.8	>38						

[a] AP = atmospheric pressure; K = 10^3 psi.

classical treatment of the problem such as used here should give correct results.

Comparison of the system vibrational frequency f with the frequency factor A for the same state indicates that the transmission coefficient from the metastable state to the emitting state is about 0.03%.

V. CONCLUSIONS

The influence of hydrostatic stress on the phosphorescence of NaI(Tl) is quite marked and it is demonstrated that the effect can be used to gain additional knowledge about the trapping sites involved. An interpretation of the effect is given which is in accord with observation and is not critically dependent upon a detailed model for the trapping site. On this basis, the change in site volume at crossover between metastable and emitting states may be determined thereby removing an ambiguity which exists in drawing configurational coordinate models for these states in the absence of detailed calculations. With additional assumptions, a description of the mechanics of the site can be given and properties of metastable states including conditions for collapse, force constants for lattice coupling, zero-point energies, and barrier transmission coefficients can be readily computed.

Assuming a Tl^+ trapping site is involved, with only symmetrical radial motion of its ligands being important, it is shown that the outward displacement of anions required for escape from the metastable state is 0.19 angstrom for the 0.66-ev trap in NaI(Tl).

The possibilities of pressure experiments on phosphors are not limited to the particular application reported here. The ability to make step-function changes in pressure allows an entire series of novel experiments to be designed. Among other advantages, transient-pressure techniques avoid much of the difficulty encountered in study of long-lived traps or other features resulting in low light output. Information on retrapping phenomena can also be obtained in this way.

It will be of particular interest to apply these methods to KCl(Tl) for which other experimental results and extensive theoretical calculations are already available. Study of prompt fluorescence efficiency and decay time as a function of pressure will provide a new test of the configurational coordinate model proposed by Johnson and Williams. Furthermore, pressure should produce opposite effects on the $^3P_2{}^\circ$ trap as compared to the $^3P_0{}^\circ$ trap for their model. A study of the prompt emission spectrum, specifically the ratio of 4750 A emission to 3050 A emission, should be very enlightening since an energy barrier of 0.025 ev between the two responsible states and displacements at cross-over of about 0.1 A are required by the Williams model. Modest pressures should produce very large changes in the intensity ratio under these circumstances. It should be emphasized that difficulties associated with the effective area of the center, i.e., the value of α, should not be important in such a test since, by hypothesis, a single center is involved. Such an experiment should therefore distinguish between this model and that suggested by Patterson and Klick, for example. The results of these experiments as well as those concerned with transient pressure effects will be reported in due course.

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