

High-pressure studies of luminescent spectra and lifetimes in alkali halides doped with Cu^+ and $\text{Ag}^{+\dagger}$

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The effect of pressure to 140 kbar has been measured on the room-temperature luminescent properties of some sodium and potassium halides doped with Cu^+ and Ag^+ . The properties studied include peak location, peak half-width, and luminescent lifetime. A signal-averaging luminescent decay apparatus is described which permits the measurement of lifetimes in the range from 50 nsec to 10 sec. The peak locations and half-widths are discussed in terms of a single-configuration coordinate model, and parameters characteristic of the potential wells are extracted. Following Kubo's picture of phonon-assisted transitions, these parameters are used to predict the change in lifetime with pressure. The agreement between experiment and calculation is reasonable. The possibilities and limitations of the analysis are discussed.

INTRODUCTION

The effect of pressure on the lifetime and steady-state emission of a phonon-assisted transition has been measured. Sodium and potassium halides doped with Cu^+ and Ag^+ were studied to quasi-hydrostatic pressures of up to 140 kbar. The pressure cell and steady-state apparatus were previously described,¹ but this paper introduces the decay apparatus. Sample preparation was identical to that described elsewhere.² The samples were made from Harshaw single-crystal alkali halides and reagent-grade monovalent dopants. (Chlorides were used for doping alkali chlorides and bromides; iodides for doping alkali iodides.) Typically, 0.05 mol% of a dopant was added to the alkali halide. The mixture was melted under vacuum in a quartz tube. All measurements were taken at room temperature (295°K). Before loading the cell, samples were annealed for 1h at 500°C and quenched to 0°C. Other precautions were taken to minimize the effect of aggregation on the data: we dealt only with

single-ion centers. Pressure effects were found to be reversible, and extrapolations to atmospheric pressure agreed with literature values.

STEADY-STATE RESULTS

The measurement of steady-state spectra has been described elsewhere.¹ For these weak transitions, it was sometimes found advantageous to replace the analog electronics with Ortec photon-counting equipment. The emitted intensity greatly decreased with pressure, but quantitative measurements of intensity versus pressure were not possible. Emission peak positions and half-widths were measured as functions of pressure for nearly all the sodium and potassium halides doped with Cu^+ and Ag^+ (see Tables I and II). Missing are NaI:Ag, KI:Ag (which does not emit),³ and NaCl:Ag (whose excitation energy is too high). Figures 1 and 2 display typical data. Peaks always shifted to higher energy, except at the potassium halide phase transition (from the fcc to the simple cubic or sc

TABLE I. Emission peak shifts. [Energies are in kilokaysers (10^3 cm^{-1}).]

Compound	Pressure (kbar)										
	0	10	18	25	30	40	60	80	100	120	140
NaCl:Cu	28.17	28.78	29.36 ^a	29.92	30.46	31.47	32.38	33.19	33.91	34.53	
NaBr:Cu	27.68	28.28	28.86 ^a	29.42	29.96	30.99	31.95	32.82			
NaI:Cu	26.64	27.22	27.77 ^a	28.28	28.76	29.61	30.33	30.91	31.36	31.67	
KCl:Cu	24.73	25.58	26.25	24.12 ^b	24.37	24.84	25.74	26.56	27.31	27.99	28.58
KBr:Cu	25.79	26.60	27.25	23.45 ^b	23.70	24.17	25.01	25.72	26.28		
KI:Cu	24.99	25.77	26.39	22.74 ^b	22.84	23.04	23.36	23.61	23.77	23.85	23.85
NaBr:Ag	38.02	38.63	39.23 ^a	39.84	40.44						
KCl:Ag	36.26	37.35	38.22	34.69 ^b	35.06	35.75	36.97	37.97	38.74	39.29	
KBr:Ag	34.78	36.06	37.09	37.05 ^b	37.10	37.20					

^a 20 kbar.

^b For the potassium halides, pressures of 25 kbar and above refer to the sc phase.

TABLE II. Emission peak half-widths. [Full width at half-maximum; energies in kilokaysers (10^3 cm^{-1}).]

Compound	Pressure (kbar)										
	0	10	18	25	30	40	60	80	100	120	140
NaCl:Cu	2.09	2.12	2.15 ^a		2.18	2.21	2.26	2.32	2.38	2.44	2.49
NaBr:Cu	1.87	1.95	2.04 ^a		2.12	2.21	2.38	2.54	2.71		
NaI:Cu	1.73	1.70	1.66 ^a		1.62	1.59	1.51	1.44	1.36	1.29	1.22
KCl:Cu	2.33	2.44	2.52	1.91 ^b	1.87	1.80	1.66	1.52	1.37	1.23	1.09
KBr:Cu	2.21	2.21	2.21	2.28 ^b	2.28	2.28					
KI:Cu	2.21	2.09	2.00	1.97 ^b	1.92	1.83	1.63	1.43	1.24	1.04	
NaBr:Ag	2.34	2.28	2.23 ^a		2.18	2.13					
KCl:Ag	3.39	3.17	2.99	2.99 ^b	2.99	3.00	3.01	3.02	3.04	3.05	
KBr:Ag	3.75	3.25	2.85	2.89 ^b	2.85	2.77					

^a 20 kbar.^b For the potassium halides, pressures of 25 kbar and above refer to the sc phase.TABLE III. Excitation peak shifts. [Energy in kilokaysers (10^3 cm^{-1}).]

Compound	Pressure (kbar)										
	0	10	18	25	30	40	60	80	100	120	130
NaCl:Cu	39.00	39.65	40.23 ^a		40.80	41.35	42.42	43.39	44.24	44.97	45.27
NaI:Cu	41.15	39.45	38.40 ^a		38.40	38.85	39.57	40.34	41.14	41.96	42.37
KCl:Cu	39.35	39.56	39.74	39.60 ^b	39.04	38.09	37.20	36.75	36.52	36.47	36.49
KI:Cu	38.09	38.48	38.79	37.26 ^b	37.15	36.92	36.45	35.93	35.38	34.75	34.40

^a 20 kbar.^b For the potassium halides, pressures of 25 kbar and above refer to the sc phase.TABLE IV. Excitation half-widths. [Full width at half-maximum; energy in kilokaysers (10^3 cm^{-1}).]

Compound	Pressure (kbar)										
	0	10	18	20	25	30	40	60	80	100	120
NaCl:Cu	4.73	4.38		4.09		3.86	3.66	3.35	3.17	3.06	3.02
KCl:Cu	4.95	5.25	5.51		6.10 ^a	5.93	5.56	4.97	4.45	4.00	3.57

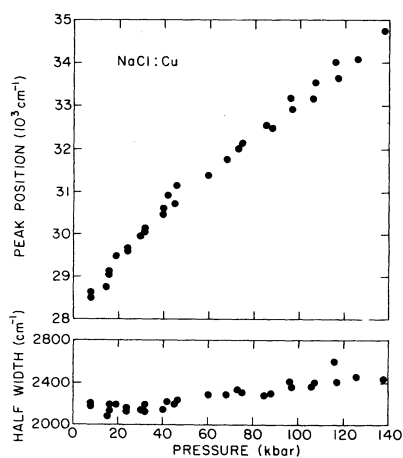
^a For the potassium halides, pressures of 25 kbar and above refer to the sc phase.

FIG. 1. Peak-shift and half-width change with pressure—NaCl:Cu.

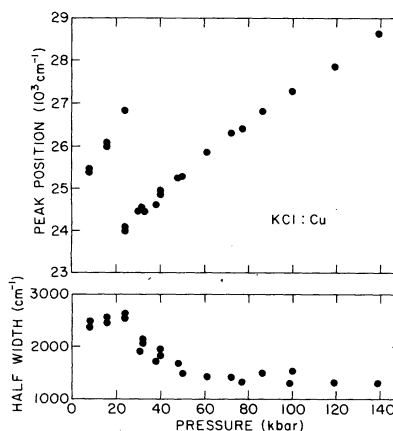


FIG. 2. Peak-shift and half-width change with pressure—KCl:Cu.

structure) near 19 kbar. Excitation was in the *A*, *B*, and *C* bands of Ag^+ or in the *D* band of Cu^+ . Tables III and IV contain data on the excitation peaks of selected phosphors. The values in Tables I–VI are from linear or quadratic fits, depending on the data. For instance, in Fig. 2, the fit to the peak shift is linear below the phase transition and quadratic above. All peaks were Gaussian without skew, and half-widths needed no correction for monochromator slit width.

DECAY APPARATUS

An apparatus (see Fig. 3) has been built which measures parameters of luminescent decay in materials under pressure. The sample is loaded in the same pressure cell as is used for steady-state measurements, and is excited by a light pulse from one of two flashlamps. The fast source⁴ has a pulse width of 20 nsec. The slow source (3- μ sec pulse width) is an EG & G FX-12 flashlamp triggered by an EG & G TM-11A.

An $f/1$ quartz lens collects the exciting light. For deep uv excitation, Schott uv-*R* interference reflection filters provide high throughput down to 220 nm. In this study, depending on the position of

the excitation peak, a filter centered at either 220, 250, or 280 nm was used. For near-uv excitation, colored-glass uv-pass filters are used. Reflected light from the pressure cell is stopped by a cutoff filter. The entire emission peak of interest (given by steady-state measurements) is passed by the emission monochromator, which is described elsewhere¹ along with the photomultiplier (PM) tube.

To select the excitation wavelength more precisely, the slow source can be used with a double monochromator; the pressure cell is then rotated 90°. However, light is at a premium, since the cell windows are $f/10$ cones with 1-mm apertures. Therefore a digitizer with memory (to be described next) was assembled to add the decay curves due to repetitive flashes.

The PM output current is converted to voltage by an RC low pass filter set at the digitizer's sampling frequency. The signal is amplified ($\leq \times 200$) by the input stages of a Tektronix 545B oscilloscope with Type *L* preamplifier. A reference PM (RCA-1P28) viewing the exciting flash provides a trigger to the Biomation 610B transient recorder, which digitizes the decay curve. An interface was built which dumps the recorder memory into a Hewlett-Packard 5400A multichannel analyzer. The interface flashes the lamp again, and a new curve is added to the old. This process is repeated up to 10^4 times at 7 Hz with the fast source of 10^2 times at 2 Hz with the slow source. For samples with lifetime $\tau < 20 \mu\text{sec}$, the fast source is used. For $0.05 < \tau < 1 \mu\text{sec}$, single-photon counting⁵ is employed, with one photon every ten flashes. The reference and signal PM's provide pulses for an Ortec 467 time to pulse height converter, which outputs to the multichannel analyzer. The fast source is flashed at 60 Hz for up to $\frac{1}{2}$ h.

When a smooth curve is built up, it is output to a teletype. A computer program fits the desired equation to the data and returns a plot. (An example is in Fig. 4.) The program is capable of decon-

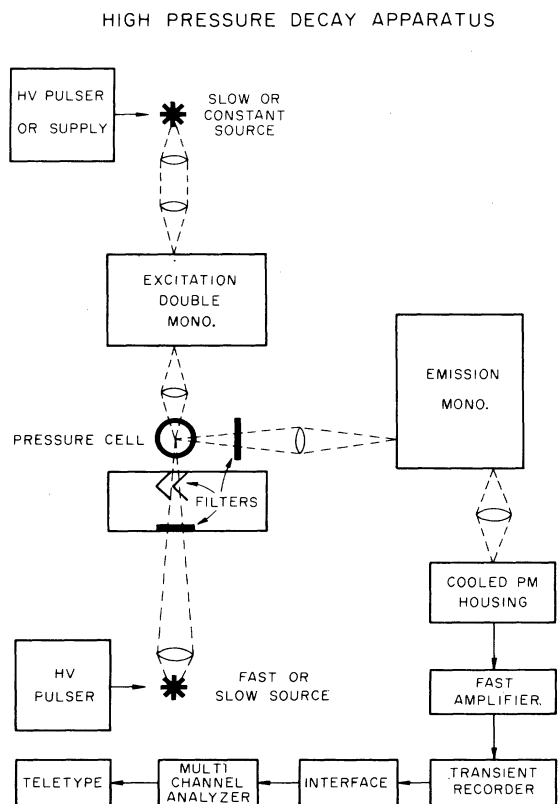


FIG. 3. Schematic diagram of apparatus for measuring the effect of pressure on luminescent decay.

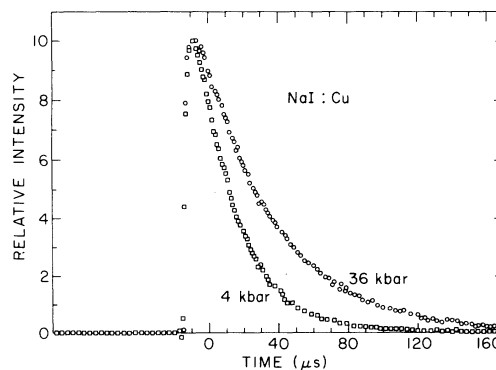


FIG. 4. Intensity vs time NaI:Cu at 4 and 36 kbar.

TABLE V. Emission lifetimes vs pressure. (Time constant in microseconds.)

Compound	Pressure (kbar)										
	0	5	10	18	25	30	40	60	80	100	120
NaCl:Cu	43.1		48.7	54.1 ^a	59.2	64.0	72.7	80.3	86.8	92.2	
NaBr:Cu	142		152	163 ^a	173	183	203	224	244		
NaI:Cu	23.8		30.1	35.6 ^a	40.2	43.9	48.7	50.0	47.7		
KCl:Cu	25.0	27.0	29.0	32.2	46.6 ^b	47.3	48.8	51.6	54.4	57.2	
KBr:Cu	91.6	101	110	125	140 ^b	144	151	167	183	198	214
KI:Cu	12.4	17.4	22.3	30.3	7.56 ^b	8.03	8.97	10.8	12.7	14.6	
NaBr:Ag	7.27		11.7	14.6 ^a	16.1	16.0					
KCl:Ag	12.3	14.1	15.8	18.6	49.9 ^b	48.7	46.2	41.4			
KBr:Ag	<1	3.87	7.53	13.4	13.2 ^b	13.9	15.3				

^a 20 kbar.^b For the potassium halides, pressures of 25 kbar and above refer to the sc phase.

volution and fitting a number of equations. All decays in this study were single exponential. To check the reproducibility of lifetime data, several pressure runs were performed for phosphors.

DECAY RESULTS

Luminescent lifetime as a function of pressure $\tau(p)$ is plotted in Figs. 5 and 6 for some phosphors. From least-squares fits to such data, Table V is constructed. A quadratic (linear) fit was employed for sodium (potassium) halide data. Due to reduced intensity, it was sometimes impossible to reach the highest pressures. While the lifetime (except in sc KCl:Ag) always increases with pressure, as does the emission peak shift, there are two noteworthy differences: (i) At all pressures, the energy of the Cu^+ peak position (except in fcc KCl:Cu) changes in the sequence $E_I < E_{Br} < E_{Cl}$. However, the Cu^+ lifetime increases in the sequence $\tau_I < \tau_{Cl} < \tau_{Br}$. In both Ag^+ - and Cu^+ -doped potassium halides, the peak position drops at the

phase transition, whereas the lifetime rises in KCl, remains constant in KBr, and drops in KI.

In a solid of optical refractive index n , an allowed transition of a localized luminescent center will have a lifetime τ given by⁶

$$1/\tau = (4e^2/9c^3\hbar^4)(n^2 + 2)n(h\nu_{em})^3 M^2, \quad (1)$$

where $h\nu_{em}$ is the emission peak position and M is the dipole matrix element. If M is constant with pressure for, e.g., NaCl:Cu, the known peak shift and refractive-index change⁷ with pressure allow a calculation of the lifetime change in 60 kbar: τ should drop by 30%. Instead, it rises by 70%. It is clear that M is not constant with pressure in this case.

There have been a number of studies of very high-pressure lifetime.^{7,8} To our knowledge, none has concerned the microsecond range of this paper. In many organics⁹ and some simple inorganics, Eq. (1) appears to describe the effect of pressure (that is, small). In our experience, the majority of

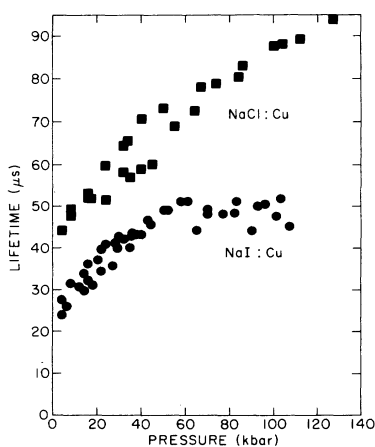


FIG. 5. Luminescent lifetime vs pressure—NaCl:Cu and NaI:Cu.

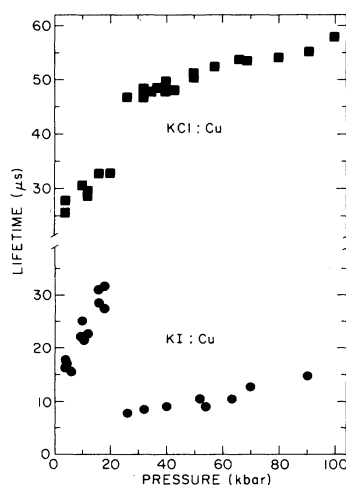


FIG. 6. Luminescent lifetime vs pressure—KCl:Cu and KI:Cu.

luminescent systems are more complicated than Eq. (1) allows, and the dynamics are strongly pressure dependent. Among the doped alkali halides, such systems include sensitized phosphors¹⁰ and Jahn-Teller split centers.¹¹ For the centers discussed here, Eq. (1) is adequate if a pressure-dependent M is used.

The Cu⁺- and Ag⁺-doped alkali halides display large lifetime changes with pressure. In general agreement with our results, lifetimes and peak shifts have been measured¹² for some of these phosphors to 6 kbar. This hydrostatic study rules out the possibility of shear strain effects in our data. Furthermore, in other studies in this laboratory¹ involving measurements of peak shifts, peak shapes, and intensities, measurements in the quasihydrostatic NaCl pressure-transmitting medium have been reproduced to 12 kbar by measurements in a truly hydrostatic medium.

DISCUSSION

The effect of pressure on localized luminescent centers in solids can best be described by a single-configuration coordinate model, where the coordinate of interest is the A_{1g} breathing mode. Applying pressure to this model leads to a set of equations¹ describing emission peak shifts and half-width changes. By comparing these equations with fits to the data, the parameters of the model are obtained. Four parameters link the ground and excited harmonic potential wells: q , the relative hor-

izontal displacement of the wells along the configuration coordinate of interest; ω^2 or ω'^2 , the force constants of the ground and excited states; $R = (\omega'/\omega)^2$; and E_{th} , the vertical energy difference between the well bottoms.

As a first approximation, we assume that ω^2 and R are independent of pressure. The pressure dependences of E_{th} and q are given by¹

$$E_{th} = E_0 + \frac{1}{2}(q + q_0)p, \quad (2)$$

$$(q - q_0)/q_0 = [(R - 1)/q_0\omega^2R]p = \alpha_b p, \quad (3)$$

where E_0 and q_0 are atmospheric-pressure values. It can be seen that vertical relative motion of the wells depends on the horizontal well displacement. Horizontal motion depends on unequal force constants (quadratic coupling). The large positive peak shifts of Figs. 1 and 2 imply that q_0 is large. (The luminescent center expands upon excitation.) The small negative curvature shows that R is a little less than one. (The excited state has a weaker force constant than the ground state.) From Eq. (3), therefore, the volume difference is large but decreasing with pressure. The volume difference q is a measure of the linear electron-lattice coupling, and it is the parameter that will affect the probability of a phonon-assisted transition.

From steady-state emission data, the model parameters R , ω'^2 , and q_0/V have been compiled in Table VI. V is the molecular volume of the alkali halide at atmospheric pressure for the fcc phase and at 20 kbar for the sc phase. When q_0 is

TABLE VI. Configuration-coordinate model parameters R , ω'^2 , and q_0 are used to calculate the lifetime change, which is compared to experiment.

Compound	Phase	R	$(\omega')^2 \frac{\text{kbar}^2}{\text{cm}^{-1}}$	q_0/V	$\tau(p_0 + 20 \text{ kbar})/\tau(p_0)^a$	
					Calculated	Measured
NaCl:Cu	fcc	0.808	1.00	0.223	1.17	1.26
NaBr:Cu	fcc	0.865	0.832	0.196	1.14	1.15
NaI:Cu	fcc	0.799	0.743	0.139	1.27	1.50
KCl:Cu	fcc	1.33 ^b	0.668	0.360	0.85	1.32
KBr:Cu	fcc	1.0	0.659	0.223	1.0	1.41
KI:Cu	fcc	0.774	0.702	0.136	1.25	2.60
KCl:Cu	sc	0.804	1.30	0.150	1.17	1.06
KBr:Cu	sc	0.646	1.58	0.108	1.33	1.12
KI:Cu	sc	0.406	7.2	0.023	1.49	1.27
NaBr:Ag	fcc	0.849	1.31	0.228	1.10	1.40
KCl:Ag	fcc	0.620	0.856	0.215	1.33	1.57
KBr:Ag	fcc	0.439	0.751	0.156	1.85	67 (2) ^c
KCl:Ag	sc	1.034	2.90	0.199	0.99	0.90
KBr:Ag	sc	0.337	78	0.011	1.11	1.22

^a All fcc values use a reference pressure $p_0 = 0$ kbar. For the sc phase, $p_0 = 20$ kbar.

^b The value of R for the fcc phase of the potassium halides depends on small changes in half-width established over a short pressure range and may not be reliable.

^c Using linear extrapolation from 8–18 kbar to discount a thermal quenching effect.

on the order of 20% of V as seen here, the electron-lattice coupling is quite strong, and the ground and excited states can have very different properties. For the sc phase of KI:Cu and KBr:Ag, q_0/V is so small that the values of R and ω^2 are not reliable.

The optical transition $d^{10} - d^9$ is parity forbidden by the Laporte rule in free Cu^+ and Ag^+ ions. The transition energy rises as the ion enters a solid, and continues to rise upon further compression, as we have seen. The lifetime remains in the millisecond range at low temperature, but as T rises, odd phonons mix electronic states of odd parity with the initial and final states, making the transition vibronically allowed. For a phonon of frequency Ω , the lifetime's temperature dependence is given by¹³

$$1/\tau = (1/\tau_0) \coth(\hbar\Omega/2kT), \quad (4)$$

where τ_0 is the $T = 0^\circ\text{K}$ lifetime.

Kubo and Toyozawa¹⁴ have described a phonon-assisted transition in terms of a configuration coordinate model. If the phonon assistance is dominated by a mode of coordinate Q_a , the dipole matrix element M is expanded

$$M(Q_a) = M_0 + M_1 Q_a + M_2 Q_a^2 + \dots \quad (5)$$

Say this mode mixes an odd level l with the excited state l'' . Then their Eq. (4.14) reduces in first order to

$$M(Q_a) = M_1 Q_a = \frac{u_{a l'' l}}{E_l^{(0)} - E_{l''}^{(0)}} M_{l'' l}^{(0)} Q_a,$$

where u is the electron-lattice coupling and E is an energy level. ($M_0 = 0$ for a transition that is strictly forbidden at the center of symmetry.) Expanding $M(Q_a)$ linearly in pressure, and assuming the elec-

tron-phonon interaction is the most pressure-sensitive factor, we find

$$\begin{aligned} \frac{M(p)}{M(p_0)} &= 1 + \frac{p - p_0}{u_{a l'' l}} \left. \frac{\partial u_{a l'' l}}{\partial p} \right|_{p=p_0} \\ &= 1 + \alpha_a (p - p_0), \end{aligned} \quad (6)$$

where p_0 is the reference pressure (0 kbar for the fcc phase and 20 kbar for the sc phase).

The breathing-mode parameter α_b of Eq. (3) is defined similarly to α_a of Eq. (6). Kubo's equation (4.12) is expanded to first order in pressure with the result (assuming ω^2 is pressure independent)

$$\alpha_b = (u_{b l'' l''} - u_{b l' l'})^{-1} \left. \frac{\partial (u_{b l'' l''} - u_{b l' l'})}{\partial p} \right|_{p=p_0}.$$

Using Eq. (6), the pressure dependence of the lifetime is

$$\begin{aligned} \frac{\tau(p)}{\tau(p_0)} &= \left(\frac{M(p)}{M(p_0)} \right)^{-2} \\ &= \left(1 + \frac{\alpha_a}{\alpha_b} \frac{(R-1)(p-p_0)}{q_0 \omega^2 R} \right)^{-2} \\ &\cong \left(1 - \frac{(1-R)(p-p_0)}{q_0 \omega^2 R} \right)^{-2}, \end{aligned} \quad (7)$$

where we have assumed that $\alpha_a/\alpha_b \approx 1$. Such an assumption will be shown to be consistent with the data, and will be more fully explained later in the paper.

In Table VI the change in lifetime over a 20-kbar pressure range (from p_0 to $p_0 + 20$ kbar) calculated from Eq. (7) is compared to the measured change. In the Cu^+ -doped potassium halides, the theory consistently underestimates the lifetime increase in the fcc phase, and overestimates the change in the sc phase. Absolute agreement is only fair, but note that within each group of phosphors, the calculated values show the same trend as the measured values. Two anomalies are found in the table, KBr:Ag (fcc) and KCl:Ag (sc), for which graphs of lifetime versus pressure are found in Fig. 7. The lifetime of KBr:Ag increases enormously from the atmospheric value,⁶ which was not predicted. Others have found that at room temperature and atmospheric pressure, the emission is quenched.¹⁵ According to steady-state data, as pressure rises, the wells move vertically so as to increase the quenching temperature, which would raise the lifetime. An extrapolation is made in Table VI which brings the measured and calculated values into agreement. Potassium halides doped with Cu^+ were found to quench at 600°K ,¹⁶ so that room-temperature quenching does not appear to be common in these crystals. In the other anomaly, KCl:Ag (sc) is the only compound where τ de-

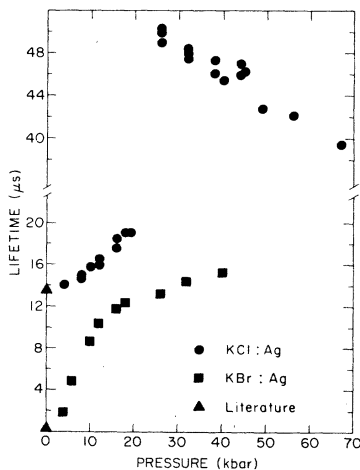


FIG. 7. Luminescent lifetime vs pressure—KCl:Ag and KBr:Ag.

creases with pressure. A small decrease was predicted from the phonon-assisted theory, but it is interesting to note that the measured drop in τ is exactly predicted by Eq. (1). This equation ties the lifetime change to the peak shift, for a simple allowed transition.

There are a number of problems with the configuration coordinate model of a phonon-assisted transition (to be referred to as the Kubo theory),¹⁴ and a host of other theories that might explain the data. Some background is necessary before these can be discussed. Only recently have a number of luminescent studies featuring decay measurements appeared.^{12, 16-21} The majority of research in noble metal-doped alkali halides has involved uv or ir absorption. The uv oscillator strength typically has the same temperature dependence as $1/\tau$ in Eq. (4). The odd phonon of frequency Ω that assists the transition is thought to be the T_{1u} resonant mode that dominates the ir absorption spectrum. In this mode, the nearest neighbors move one way, while the impurity ion moves in the opposite direction with large amplitude.¹³ One might not expect hydrostatic pressure to couple to such a nontotally symmetric vibrational mode, but the force constant of the T_{1u} mode in NaCl:Cu was found to nearly double in 6 kbar.²² (The force constant Ω^2 should be linearly related to τ at room temperature through the mean-square displacement $\langle Q^2 \rangle$ by²³

$$1/\tau \propto \langle Q^2 \rangle = kT/\Omega^2, \quad (8)$$

so that the lifetime should increase with pressure. The increase is observed, though for NaCl:Cu τ certainly does not double in 6 kbar.) It is clear then that pressure couples to the T_{1u} mode. A measure of the coupling is the ratio α_a/α_b of Eq. (7), which must be approximately unity in order to achieve the consistent results of Table VI. From the definition of α , the ratio is unity if the logarithmic derivatives with pressure of u_{jmn} are equal for both normal modes $j=a$ and b , independent of the electronic states m and n ; that is, if the change with pressure of the electron-phonon interaction of a mode is proportional to the strength of the interaction, and the breathing and resonant modes have the same proportionality constant. That $\partial(\ln u_{jmn})/\partial p$ does not depend on the symmetry of the j th mode is a surprising result that should be investigated further.

The lifetime or oscillator strength may not obey Eq. (4); the results are explained by higher-order phonon assistance or static lattice distortions. A small ion replacing a large ion might not be most stable at the center of symmetry. Its off-center position continuously breaks the Laporte rule. One would expect the oscillator strength (or inverse lifetime) to be large and temperature independent.

Such behavior is seen in absorption with NaI:Cu,²⁴ and the Cu⁺-doped potassium halides.²⁵ In emission, KI:Cu is off center, but there is controversy about NaI:Cu.^{20, 21} The other compounds discussed here are on center, though they may not obey Eq. (4) due to higher-order electron-lattice terms.^{21, 26}

It has been theorized²⁷ (and confirmed in KCl:Li)²² that the application of pressure, by decreasing the volume available to the substituted ion, will cause off-center to on-center transitions. At low temperature, such a transition would cause a large rise in the lifetime. However, on- and off-center ions have similar lifetimes at room temperature (e.g., the Cu⁺-doped iodides²⁰), and similar temperature dependences down to 100°K,²¹ so that the off-center effect does not dominate room-temperature emission studies. (This is not true for absorption.) It can only explain the unusually large increase in τ with pressure in KI:Cu (fcc), which is off center at atmospheric pressure and might be going on center with pressure. It is not clear whether the potassium halide phase transition favors an on- or off-center position, since the lattice constant increases by 5% while the volume drops by 13% as the coordination number changes from 6 to 8.

Though the other compounds are on center at room temperature, some exhibit off-center distortions at low temperature, so that the assumption of harmonic potential wells in the Kubo theory is not strictly true. In addition, the higher than linear terms in Eq. (5), which are sometimes necessary to describe the temperature dependence of τ ,²¹ are not included in the Kubo theory. The Kubo theory predicts $\tau(p)$ to have an upward curvature, while the observed curvature is frequently downward. This discrepancy can be attributed to the linear approximation. Indeed, if there were no quadratic electron-lattice interaction, R would be one.

Another problem, worse in Jahn-Teller studies,^{1, 2} is that the state to which the center is excited in absorption is not necessarily quite the same as the state from which emission occurs. The large values of q ($q_0/V \sim 20\%$) and large Stokes shifts ($>10^4$ cm⁻¹ for Cu⁺-doped alkali halides) demonstrate this fact. Because of the increased volume of the relaxed excited state, an off-center position is only stable in KI:Cu, whereas in the ground-state NaI:Cu and the Cu⁺-doped potassium halides are all off center. Thus the lifetime predicted from the oscillator strength can be orders of magnitude faster than the measured lifetime if an off- to on-center transition occurs upon excitation. Even when both ground and excited states are on center, the optical transition can be 10–100 times more allowed in absorption than emission.¹⁹

The configuration-coordinate model, which con-

siders two similar harmonic states, must therefore be employed cautiously. Model parameters were found from emission data, since equations using excitation or Stokes-shift data yielded inconsistent parameters. This paper, then, is a pressure study of the excited state. With all its pitfalls, the configuration coordinate model produces reasonable and smoothly changing parameters (see Table VI). And the Kubo theory, which incorporates these parameters, predicts lifetime changes with pressure that correlate with the measured changes.

One final problem with the configuration-coordinate introduces some alternative theories of the effect of pressure on lifetimes. For an allowed transition, the Condon approximation is generally made, setting $M(Q) \approx M_0$ in Eq. (5). This allows one to eliminate the Franck-Condon factors⁶ and arrive at Eq. (1). In this case, one cannot relate lifetime changes to changes in vibrational overlap integrals, as is sometimes done.^{8,12} For a forbidden transition, however, the Condon approximation may be invalid, since M depends strongly on the odd coordinate Q . An equation was derived²⁸ to predict $\tau(p)$ for this case:

$$\frac{1}{\tau} = \frac{1}{\tau_0} \coth \frac{\hbar\Omega}{2kT} + \frac{M_1^2 p^2}{\omega^4}. \quad (9)$$

Unfortunately, (9) predicts a decrease in τ , as does a consideration of Franck-Condon factors, whereas τ was found to increase with pressure.

In other theories, the effect of pressure on lifetimes is ascribed to shifting energy levels. If the lifetime in Cu⁺-doped potassium halides is governed by a metastable level,²⁹ pressure would change τ through the trap depth. However in the Ag⁺-doped alkali halides, where there is no metastable level, the lifetime has the same pressure dependence. In another theory, the amount of configuration interaction (mixing) caused by odd phonons is determined solely by the energy difference between configurations. The lifetime is proportional to the square of the energy difference, which would change with pressure. There is no direct measure

of energy differences in the relaxed excited state. One must rely on levels measured by absorption as a function of lattice constant,^{30,31} since there is no pressure study of uv absorption. Then is the d^{9s} state mixes primarily with the d^9p state, τ would decrease with pressure, while if mixing with charge-transfer bands were predominant, τ would increase with pressure. One cannot place much faith, however, in such an extrapolation of absorption to emission and composition to compression.

SUMMARY

Measurements of luminescent lifetime as a function of pressure have been found useful in studying processes that compete with luminescence, such as trapping, thermal quenching, and resonant energy transfer. We have shown here that the intrinsic radiative lifetime can change with pressure. Compression of the breathing mode couples to the odd phonon which assists the forbidden transition in Cu⁺- and Ag⁺-doped alkali halides. Steady-state emission measurements are interpreted by a configuration-coordinate model, which predicts that pressure will decrease the phonon assistance. The measured lifetimes are found to increase, in agreement with the predictions. While the model has a number of limitations, other theories are found to be inadequate to explain the data.

This study suggests other possible experiments. The effect of pressure on the uv oscillator strength would be the most useful but very difficult. Pressure studies at temperatures below 100°K could examine static lattice distortions. In nonpressure studies, two areas stand out. First, the CsCl (sc) structure has been ignored, except for the discovery of off-center CsBr:Ag.³² This makes pressure studies difficult to interpret, since most of the alkali halides have the sc structure at high pressure. Second, the excited state is very poorly characterized, both experimentally and theoretically, compared to the ground state. It is hoped that this paper will help to rectify that situation.

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