ANOMALOUS THERMOLUMINESCENT KINETICS OF
IRRADIATED ALKALI HALIDES

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In a previous work\textsuperscript{1} we reported isothermal decay characteristics and kinetic order of alpha-irradiated Harshaw Optical Grade NaCl, KCl, and KBr. The NaCl and KBr showed first-order kinetics, whereas KCl showed a kinetic order of $3/2$; the results for NaCl and KBr were in accord with earlier views.\textsuperscript{2} Further investigation by us has revealed a more complex behavior for the same three salts obtained from other sources.\textsuperscript{3} An apparent kinetic order of less than one was found for all three salts and was common to nearly all the sources.\textsuperscript{4} Such anomalous kinetics (less than first order) indicate that more than a single process is involved. It is believed that the anomalous kinetics are associated, in part, with the absence of OH$^-$ ions in the crystals.

Single crystals were irradiated in the as-received condition at room temperature using either 10-MeV protons, 40-MeV alphas or 2-MeV electrons; the kinetic results were found to be independent of the irradiation particle over the range of flux levels employed ($10^{14}$ to $10^{17}$/cm\(^2\)). For flux levels of $10^{14}$/cm\(^2\) or greater, only one glow peak resulted in the temperature range of 25 to 300\(^\circ\)C; furthermore, the peak was composed of a single spectral band.\textsuperscript{5} The kinetics were investigated by means of isothermal annealing near the previously determined glow peak temperature; the total intensity of the luminescence $I$ was measured as a function of time $t$. 
If a single process were involved,

\[ I = \frac{-dC}{dt} = \gamma_1 C^n \quad \text{(at const temp.)} \]  

(1)

where \( C \) is the concentration of reacting centers, \( \gamma_1 \) is the rate constant, and \( n \) is the kinetic order (0, 1/2, 1, etc.). It can be shown for Eq. (1) that a plot of \( \log I \) versus \( t \) should be a straight line if \( n = 1 \), and a plot of \( I^{(1/n-1)} \) versus \( t \) should be a straight line if \( n \neq 1 \). Typical data (Fig. 1) show that \( n \neq 1 \); the direction of curvature indicates \( n < 1 \). Since the actual value for \( n \) is 0.7 ± 0.1 (obtained from plots of \( I^{(1/n-1)} \) vs \( t \)), \( n \) should be interpreted only as an apparent kinetic order in the present investigation.

A simple model (Fig. 2) for explaining such behavior consists of two competing processes; a first-order radiative one (solid lines) and a zero-order radiationless transition (dashed line). For such a model

\[ \frac{-dC}{dt} = \gamma_1 C + \gamma_2 \quad \text{(at const temp.)} \]  

(2)

where \( \gamma_2 \) is the zero-order-rate constant. The exact nature of the zero-order process is not clear. The emission process, however, is somewhat better understood, the intensity being given by the equation

\[ I = \gamma_1 C \quad \text{(at const temp.)} \]  

(3)

It should be noted that for our model \( I \neq -\frac{dC}{dt} \). Combining Eq. (3) with the integrated form of Eq. (2) yields

\[ -\ln(I + \gamma_2) = \gamma_1 t + K \]  

(4)

where \( K \) is the constant of integration. With proper choice of \( \gamma_2 \), Eq. (4) fits the present data as well as, if not better than, the plot,
\( I^{(1/n-1)} \) versus \( t \). The values of \( y_1 \) and \( y_2 \) obtained in this manner for a particular temperature vary slightly from crystal to crystal. However, it may be stated that approximately 30\% of the total decay proceeds by the zero-order process.

Certain experimental results (at least for NaCl) indicate that the anomalous kinetics are associated with the absence of OH\(^-\) ions:

1. Not all samples for which \( n < 1 \) were examined for OH\(^-\) content, but the ones that were examined showed essentially no OH\(^-\) absorption band.
2. Harshaw NaCl that had been heat treated in an HCl atmosphere to neutralize the OH\(^-\) ions had no OH\(^-\) absorption band and showed \( n < 1 \).
3. NaCl samples, normally showing \( n < 1 \), showed as high as \( 3/2 \)'s-order kinetics as well as the OH\(^-\) absorption band, after being heated near the melting point in moist argon for 48 hr. The variability of order from source to source in this latter case indicates that the OH\(^-\) ion may not be the sole entity involved.

A more detailed study of the impurity effects is now in progress.
FOOTNOTES


4. The exceptions were: Semi-Elements KCl, 3/2's order (ref. 1); Optavac KBr and Semi-Elements KBr and KCl, variable (essentially 1st or less than 1st).

5. Semi-Elements KBr showed two spectral bands.

6. A straight line plot of log I vs. t would also result from a process where \( I = \frac{-dC}{dt} = \gamma_1 C + \gamma_2 \).

7. Our model would require the radiationless transition to be inhibited by the presence of OH\(^-\) ions.


10. Other species may be divalent metal ions or other oxygen bearing anions. The O\(^-\)\(_2\) band has been reported to accompany the OH\(^-\) band; D. A. Patterson, Phys. Rev., 127, 1564 (1962).
Fig. 1. Isothermal decay of NaCl showing apparent kinetics of less than first order ($T = 265^\circ C$).

Fig. 2. Model of process.