ity, it follows that the transitions persist for such potentials.

(ii) An extra feature of real three-dimensional fluids that is absent in our one-dimensional models is the occurrence of a solid-liquid transition. Perhaps our anticipated second critical point (P_2, ρ_2, T_2) materializes within the solid region, giving rise to a solid-solid transition that involves no change of crystal symmetry.[11] This seems more likely to us than the possibility that the "extra" transition could play a fundamental role in determining the characteristics of the solid-liquid transition itself.

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[1] In three dimensions, presumably any finite-range attraction suffices to guarantee a phase transition. In one dimension the negative potential must be long ranged in some extreme sense, for instance, decaying like $-r^{-n}$ with $1<n<2$ [F. J. Dyson, Commun. Math. Phys. 12, 91, 212 (1969)]. In all dimensions a weak long-ranged attraction of the form (1) yields a first-order transition in the limit $\gamma \to 0$. [See J. Lebowitz and O. Penrose, J. Math. Phys. 7, 98 (1966). See also M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, *ibid.*, 4, 216 (1963), and N. G. van Kampen, Phys. Rev. 135, A362 (1964), for closely related earlier work, and D. J. Gates and O. Penrose, Commun. Math. Phys. 15, 225 (1969), for closely related recent work.]

[2] See J. Rowlinson and B. Widom, J. Chem. Phys. 52, 1670 (1970), for a detailed discussion of this symmetry.

[3] A greater variety of transitions can be expected for $\nu > 1$. Consider, e.g., the two- or three-dimensional (cubic) lattice gas with a finite nearest-neighbor repulsion V_0 and no attraction. Then there are two second-order transitions (antiferromagnetic in spin language) below a critical temperature (the Néel temperature). By adding an attraction of the type (1), one obtains four transitions along low-temperature isotherms.

[4] Lebowitz and Penrose, Ref. 2; Kac, Uhlenbeck, and Hemmer, Ref. 2; van Kampen, Ref. 2; and Gates and Penrose, Ref. 2.

[5] J. F. Nagle, to be published. We are grateful to Dr. Nagle for receiving a preprint before publication.

[6] See the articles by H. Takahasi and L. Van Hove, in *Mathematical Physics in One Dimension,* edited by E. H. Lieb and D. C. Mattis (Academic, New York, 1966).

[7] J. Rowlinson, *Liquids and Liquid Mixtures* (Butterworths, London, 1969), p. 86. H. D. Baehr, Forsch. Ingenieurw. 29, 143 (1963), and Brenstoff Wärme Kraft 15, 514 (1963). We are grateful to Dr. J. M. H. Levelt Sengers for making copies of Baehr's articles available to us.

[8] The exponent $1-\alpha'$ in Eq. (7) is just $1/s$ in our model and could equally well be expressed as 2β or $2/(\delta-1)$. It is, however, only the exponent $1-\alpha'$ that one might expect to carry over to real fluids, since fluid values of 2β or $2/(\delta-1)$ are inconsistent with the experimental indications that the exponent must be close to unity. Eq. (7) was also conjectured in Ref. 2 on the basis of a very different model.

[9] B. Widom, J. Chem. Phys. 43, 3098 (1969).

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[11] Such transitions are known to exist. See, for example, A. Jayaraman, Phys. Rev. 137A, 179 (1965).

THERMOLUMINESCENCE OF KCl:Tl BETWEEN 30 AND 400°C DETERMINED BY SIMULTANEOUS INTENSITY AND SPECTRAL DISTRIBUTION MEASUREMENTS*

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The thermoluminescence of KCl:Tl following gamma-ray irradiation was studied using a new technique. Most of the emission occurs at 3050 Å, but three weak bands also appear. The 3050-Å glow curves, after different doses, consist of one or more peaks from a set of seven peaks occuring between 312 and 537°K. The total 3050-Å emission increases and then decreases, and the most intense glow peak shifts from low to high temperature with increasing dose.

Crystals of KCl:Tl have been intensely studied both theoretically and experimentally for more than 20 years.[1,2] In fact, this particular combination of host alkali halide and intentionally introduced impurity probably has been investigated more extensively than any other similar combination. A large fraction of the experimental work, involving almost every conceivable kind of solid-state technique, has been confined to measurements at room temperature or below. In contrast, only a few cursory measurements of the KCl:Tl thermoluminescence above 20°C have been published.[3-5] Reported below are the principal results of a comprehensive study of the thermoluminescence, between 30 and 400°C, from KCl:Tl crystals after Co^{60} gamma-ray irradiation.

Gamma-ray irradiation of KCl:Tl crystals produces large concentrations of *F*, *M*, *V*-region, and other color centers, i.e., increases the trapped-charge concentration, changes the ionization state of the substitutional Tl^+ ions, and presumably introduces lattice defects.[6,7] Recent chemical studies indicate that gamma-ray irradiation converts Tl^+ to both Tl^{++} and Tl^0 species which are stable at room temperature and above.[8] Annealing experiments indicate that the effects of irradiation are almost completely removed by heating the crystal to 400°C.[7,9] Specifically, the color centers disappear and the initial Tl^+ concentration is restored. Thus, thermoluminescence measurements in the 30 to 400°C range should provide direct information on the redistribution of charge occurring during irradiation and annealing.

In a typical "glow curve" obtained with a conventional thermoluminescence spectrometer the ordinate usually is proportional to the photomultiplier current. Since the phototube is exposed to the entire luminescent spectrum, the current represents an integration over the emission spectrum that is weighted according to the wavelength response of both the phototube and other parts of the apparatus. Thus, a single glow peak may contain contributions from two or more emission bands. Furthermore, the number of bands contributing to the different glow peaks may change as the temperature changes. Usually these thermoluminescence curves are analyzed by applying, one after another, a series of increasingly complicated kinetic models until a reasonably good "fit" is obtained. Clearly, it is advantageous to have thermoluminescence data which include both emission-spectrum and intensity information. It is particularly advantageous to have glow curves describing the emission from a single luminescent center.

The results on KCl:Tl described below were obtained from a study which employed, for the first time, recently completed apparatus con-

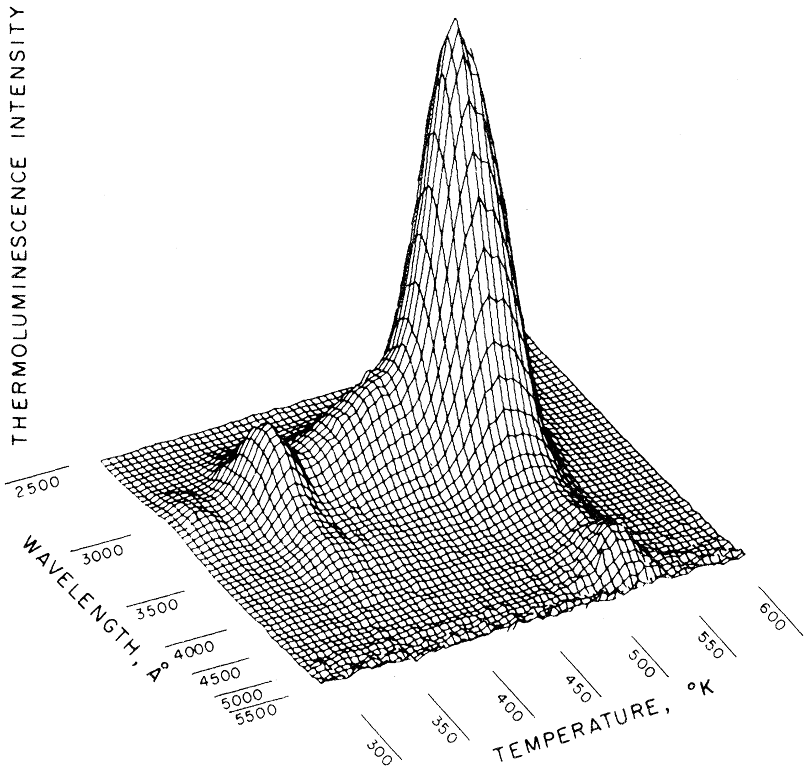

FIG. 1. A "three-dimensional plot" of the thermoluminescence from a KCl:Tl crystal containing approximately 100 ppm Tl^+, after it had been exposed to a dose of 3×10^7 rad of Co^{60} gamma rays. The sample was heated linearly at approximately 10°C/min.

taining several unique and powerful features. Very briefly, this equipment simultaneously measures both the intensity and spectral distribution of the thermoluminescence emission. The data are computer processed and a plot, such as is shown in Fig. 1, is obtained from each sample. The sample is heated in a vacuum at a linear rate, usually 10°C/min, using an electronically regulated oven controlled by a bridge circuit containing a platinum sensor in one arm, and a digitally produced resistive ramp in the other. Each line parallel to the wavelength axis represents 32 scans, at a rate of 1 scan/sec, of a grating spectrometer. The intensity versus wavelength information for each scan is stored in a 1024-word buffer in a small computer programmed to accumulate data using well-established "signal averaging" techniques. The data averaged over 32 scans, representing a temperature interval of approximately 5°C, are then stored on magnetic tape. Each "glow spectrum", which may consist of up to 66 000 points after averaging, is processed on a large computer. This procedure includes the required normalization and calibration corrections, and preparation of the three-dimensional plots whose perspective may be altered to obtain views which emphasize the dependence on either temperature or wavelength. It should be emphasized that all of the data are obtained from a single sample after a single irradiation period. Clearly, a plot like Fig. 1 is a very graphic device for presenting thermoluminescence data, but more important, it facilitates a rapid and a thorough analysis of the data. Parenthetically, it should be mentioned that these plots show how to maximize the sensitivity of conventional thermoluminescence apparatus for the study of individual emission bands in weakly emitting samples. Specifically, they provide the data required to specify the maximum band-pass optical filter which can be used and still eliminate unwanted emission. This apparatus will be described in a separate paper.

All measurements were made on previously unirradiated pristine samples cleaved from a single boule of KCl:Tl containing approximately 100 ppm of Tl which had been purchased from Harshaw. This thallium concentration is low enough to prevent the formation of all but a negligible quantity of thallium dimer. Each sample was wrapped in light-tight aluminum foil for all operations prior to heating. They were irradiated with Co^{60} gamma rays at a dose rate of approximately 5×10^5 rad/h at approximately 25°C. The crystals were subjected to total doses between 10^5 and 5×10^8 rad. Because the thermoluminescent emission close to room temperature depends on the time interval between the termination of the irradiation and the start of the measurements, the data were obtained from glow curves started 24 h after irradiation.

A comparison of the "three-dimensional" plots obtained from the irradiated samples reveals several general features. First, a large fraction of the emission is confined to a broad band which peaks at approximately 3050 Å. There are additional bands at 3800, 4400, and 4750 Å. All of these bands correspond closely to the emission bands previously observed in KCl:Tl.[6,10-12] The bands at 3800, 4400, and 4750 Å do <u>not</u> occur at all temperatures and their presence makes it difficult or impossible to analyze conventional glow curves. Second, there are seven distinct glow peaks associated with the 3050-Å band over the dose and temperature range examined. Third, at low total doses most of the emission is confined to low-temperature glow peaks. As the total dose is increased the total amount of light emitted increases and the distribution of emitted light among the various glow peaks shifts towards higher temperatures. Finally, in samples exposed to 5×10^8 rad or more, the emission is reduced and confined to the highest-temperature peaks.

To determine, if possible, the thermoluminescence kinetics, plots were prepared showing the emission at 3050, 4400, and 4750 Å as a function of crystal temperature. All of these constant-wavelength glow curves were immediately analyzable using the simplest conceivable kinetics. Namely, each of the traps appears to be independent of the others, i.e., retrapping does not occur, and the untrapping rates are all given by the simple expression $dN/dt = N_0 s \exp(-E/kT)$, where N_0 = initial trapped-charge concentration, s = frequency factor, E = activation energy, and k and T have the usual meaning. A typical 3050-Å glow curve and its constituent glow peaks are shown in Fig. 2.

Most importantly, all of the 3050-Å glow curves obtained after irradiations extending from 10^6 to 5×10^8 rad can be fitted by 7 peaks; only the relative intensities of the various peaks change from one curve to the next. The parameters describing low peaks producing the 3050-, 4400-, and 4750-Å bands in a crystal exposed to 3×10^7 rad are contained in Table I.

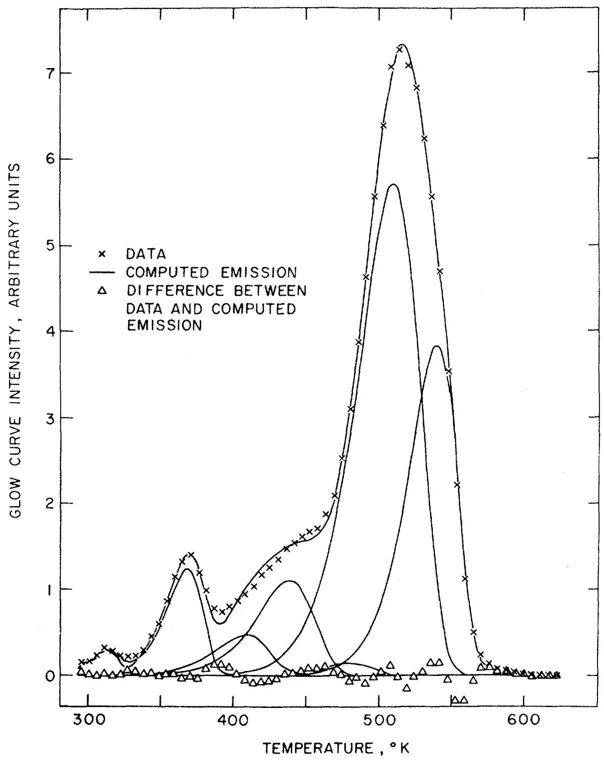

FIG. 2. A "constant-wavelength glow curve," i.e., a plot of luminescent intensities versus temperature, made in this instance by taking a "cut" through the three-diminsional plot at 3050 Å. This crystal had been subjected to a dose of 3×10^7 rad. Also shown are the individual glow peaks obtained by the simple kinetic analysis described in the text, as well as a curve indicating the difference between the observed data and the computed glow peaks.

The data on the emission spectrum as a function of temperature can be used to obtain information on the electronic processes responsible for the light emission. The 3050-Å emission band corresponds to a transition specifically attributed to Tl^+ ions substituted at cation sites, and as mentioned above, the other bands are included in previous reports on luminescence in KCl:Tl.[6,10] These results and recent theoretical arguments[13] indicate that it may be possible to construct a classical one-dimensional configuration-coordinate diagram describing some of the absorption and emission transitions associated with this center. All of the necessary information can be obtained from the thermoluminescence emission-spectra data and recent optical-absorption measurements showing that the triple-degenerate Tl^+ *A* band can be resolved into three Gaussian-shaped components.[14] The resulting configuration-coordinate diagram is shown in Fig. 3. The absorption by the lowest-energy component of the *A* band and the subsequent emission of the 3050-Å band at room temperature computed from the diagram is shown in Fig. 4. The latter figure also contains the corresponding measured spectra. The fit is as good as can be expected. Furthermore, the var-

Table I. Thermoluminescence "glow peaks" in KCl:Tl after a 3×10^7-rad gamma-ray irradiation.

Emission band (Å)	Glow peak temperature (°K)	Activation energy (eV)	Frequency factor (sec^{-1})
3050	312	0.81	2.0×10^{11}
	367	0.89	1.9×10^{10}
	407	0.73	9.0×10^{6}
	438	0.80	1.2×10^{7}
	480	1.18	2.6×10^{10}
	509	1.11	8.1×10^{8}
	539[a]	1.70	8.5×10^{13}
4400	537[a]	1.39	1.0×10^{11}
4750	541[a]	1.66	3.9×10^{13}

[a] These three emission bands could arise from charge release from a single trap.

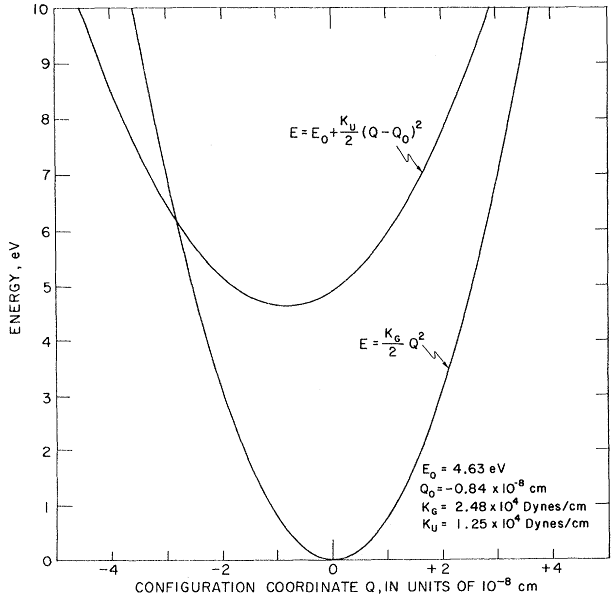

FIG. 3. A classical one-dimensional configuration-coordinate diagram describing the absorption and emission of substitutional Tl^+ ions in KCl. The diagram applies to absorption by only the lowest-energy component of the Tl^+ *A* band and subsequent emission at 3050 Å.

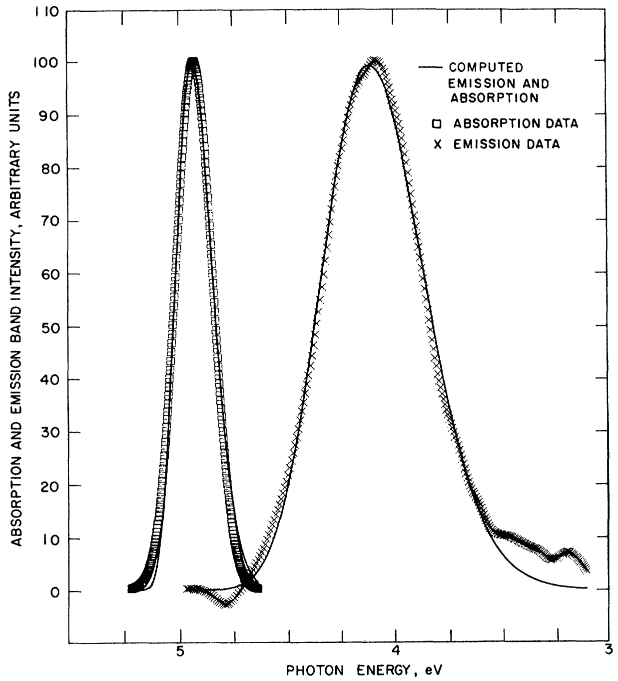

FIG. 4. The experimentally determined emission and absorption spectra, described in the caption for Fig. 3, and the corresponding spectra computed from the configuration-coordinate diagram.

iations in the width as a function of temperature of both the lowest-energy *A* absorption band and the emission band agree reasonably well with the available data. However, it has not been possible to construct a one-dimensional configuration-coordinate diagram describing the absorption in the other two components of the *A* band and subsequent emission by the 3050-Å band. It could be that it is impossible to approximate this last mentioned situation by a one-dimensional diagram. Alternatively, absorption by the higher-energy components populates higher energy levels which could decay to the lower level leading to the 3050-Å emission.

Ultimately, one would hope to specify the nature of the charge trap producing each of the observed glow peaks. Almost certainly this would require data from other than thermoluminescence measurements. Also, it is necessary to explain how the KCl:Tl thermoluminescence depends on dose. Some speculative explanations are suggested by these data but there is insufficient space to discuss them here.

In summary, these results provide what appears to be a complete characterization of the traps that contribute to the luminescent emission at 3050 Å from KCl:Tl crystals irradiated at room temperature and then heated. Furthermore, they demonstrate that the simultaneous determination of emission intensity and spectral distribution is a particularly useful technique for studying thermoluminescence.

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†Guest scientist at Brookhaven National Laboratory.

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