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High-pressure optical studies of doped alkali halides. II. Jahn-Teller effects*

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The emission spectra of heavy-metal–doped alkali halides exhibit a doublet in some temperature ranges at 1 atm. This splitting results from the Jahn-Teller effect which gives excited-state minima corresponding to a tetragonal (A_T) and a rhombic (A_X) distortion. The latter lies lower in energy. The effect of pressure has been studied on the shifts of the emission peaks and the relative occupations of the two states for various alkali halides in both the NaCl and CsCl structures doped with Tl^+, In^+, and Ga^+. In general, the effect of pressure is to increase the occupation of the higher-energy (A_T) state at the expense of the A_X state. This redistribution is explained in terms of the difference in the pressure shifts of the A_T and A_X peaks and the possible effect of this difference on the barrier to thermal transfer between the minima. A few remarks are included on pressure effects on the Jahn-Teller splitting in absorption spectra.

In this paper we discuss the effect of pressure on Jahn-Teller–split spectra of heavy-metal ions in alkali halides; our primary concern will be with the luminescence spectra. The methods of sample preparation and the high-pressure techniques are discussed elsewhere.[1]

The problems in using a simple configuration-coordinate model to describe the optical transitions of localized centers in heavy-metal-doped alkali halides are essentially due to three interrelated effects. First, the assumption that a single configuration coordinate, the totally symmetric A_{1g} coordinate, can describe the relevant electronic states is incorrect. Second, in the simplest description, the Born-Oppenheimer approximation cannot include electronic degeneracy. The p-like excited electronic state contains such electronic degeneracy. Third, the Tl^+ ion has a large spin-orbit coupling parameter, and the ion's interaction with its environment must be treated in the intermediate-coupling regime; the configuration-coordinate description for localized states is intended to describe impurity or defect systems which couple fairly weakly with the host environment. These three conditions are important to a complete description of the electronic states of KCl : Tl-type phosphors.

The importance of the interactions between the impurity electronic system and non-totally-symmetric lattice distortions is manifested in at least three types of measured phenomena. Raman scattering spectra of Tl^+-doped alkali halides indicate strong coupling of the Tl^+ ion to vibrational modes of symmetry E_g and T_{2g}; in fact, these vibrations dominate the scattering spectra.[2,3] Second, it has been shown that fine structure exists in the A-, B-, and C-absorption bands in the doped alkali halides and that this structure may be attributed to Jahn-Teller distortions of the impurity complex. In addition, structure has been observed in the luminescence caused by A-band excitation; this structure has also been described in terms of the Jahn-Teller effect (JTE). The effect of high pressure on the luminescence is the subject of this paper, but a few remarks on the absorption spectra are included first.

ABSORPTION

A theoretical explanation of the observed fine structure of the A and C bands in absorption was given by Toyazawa and Inoue in terms of the dynamic JTE.[4] Since then, several workers have investigated the structure of these bands.

We mention here only a few results on KCl, KBr, and KI doped with In^+, as determined from excitation spectra. In the low-pressure NaCl phase we observed an increase in A-band splitting δ_A with pressure qualitatively similar to that observed by Masunaga and Matsuyama.[5] At the transition (near 19 kbars) the splitting decreases by 250–300 cm^{-1}. In the high-pressure CsCl phase, the splitting δ_A increases for KCl : In and KBr : In, but decreases slightly for KI : In.

The change in splitting δ_A with pressure is small compared to the overall shift of the average A-band energy with pressure so that, except at the phase transitions, one observes essentially no change in the structure of the spectra up to 130 kbars. The computer resolutions of the A doublet indicate no significant change with pressure in the relative areas under the A_1 and A_2 bands.

EMISSION

The presence of Jahn-Teller interactions in the relaxed excited state from which luminescence occurs in heavy-metal-doped alkali halides is indicated by the existence of an emission doublet during A-band excitation of KI : Tl, as first observed by Edgerton and Teegarden.[6] Since that study, the emission doublet from A excitation has been observed at various temperatures in a number of the NaCl-structure alkali halides, doped with Tl$^+$, In$^+$, Ga$^+$, Sn^{++}, and Pb^{++}, all of which have outer electron configurations (ns^2). A review of the temperature phenomenology of the doublets in the various materials is given by Fukuda.[7] He proposed a model which described most of the observed features of the luminescence excited in the A band. This model predicts the coexistence of two types of minima on the ${}^3T_{1u}$ excited-state adiabatic potential-energy surface (APES) in the subspace of tetragonal lattice distortions. The coexistence of the two minima is a result of both the JTE and the spin-orbit interaction, which may be rather large for Tl$^+$ ($Z=81$).

Two minima occur on the ${}^3T_{1u}$ APES in the E_g subspace, where the tetragonal distortions of symmetry E_g are denoted Q_2 and Q_3. These minima lead to an emission doublet, which can be resolved into two bands, labeled A_T (high energy) and A_X (low energy). The so-called T minimum on the excited-state APES represents a tetragonal lattice distortion and results in the A_T emission band. The A_X emission is from the (doubly degenerate) X minima, which are probably of rhombic symmetry (nearly tetragonal).

Fukuda suggests that the A_T emission is conjugate to the A absorption; that is, the A_T emission is the inverse process of the A-absorption and can be represented schematically as ${}^3P_1 \rightarrow {}^1S_0$. This assumption is used throughout and implies that A excitation occurs in a region of the APES near the T minimum. However, the A-absorption and A_T emission bands do not have the same directions of pressure shifts[1] so that the two transitions are not described by a single-configuration-coordinate model. The trigonal modes have been shown to play a major role in the absorption spectra, while the A_T emission occurs from a tetragonally distorted state. The states absorbed to and emitted from are not represented by a single excited-state harmonic well along any of the coordinates and, in particular, not along the volume coordinate Q_1.

Fukuda's original model has been extensively modified by Ranfagni, Viliani, *et al.*[8–13] In spite of these recent treatments which yield more comprehensive and complex interpretations, the essential results can be simply stated: For a rather wide range of semiempirical parameters, in basically all of the known experimental systems of KI:Tl-like phosphors, there exists the possibility of the coexistence of two kinds of minima on the ${}^3T_{1u}$ APES accessible by A excitation. These minima lead to the so-called A_T and A_X emission bands. On the basis of this result, the temperature and pressure dependences of the emission bands can be explained.

Cross sections of the ${}^3T_{1u}^*$ APES's along Q_3 are shown in Fig. 1, along with the ground-state APES cross section. The nondegenerate ground-state well has its minimum at $Q_2 = Q_3 = 0$. The relevant features are the existence of the T^* minimum, the saddle point S, the doubly degenerate X minima at an energy below the T^* minimum, and a thermal potential-energy barrier between the T^* and X minima. Optical excitation in the A band occurs from the ground state to a region of the excited-state APES near the T^* minimum; vibrational relaxation occurs, leaving the system at the T^* minimum. That is, A excitation preferentially populates the T^* minimum.[7] At low temperatures (depending on the particular system), the system is frozen into the T^* minimum, and only the high-energy A_T emission results. As the temperature is raised, the thermal barrier can be overcome, and a sufficient probability exists for the system to relax radiationlessly to the X minima. Thus, with increasing temperature, the emission occurs less and less in the A_T band and more in the A_X (lower-energy) band. At sufficiently elevated temperatures (depending again on the particular system), the emission occurs

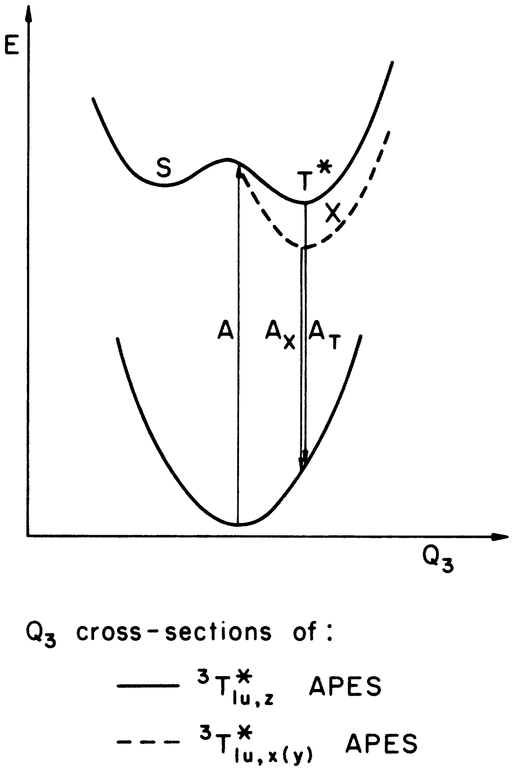

FIG. 1. Cross section of ${}^3T_{1u}^*$ adiabatic potential-energy surface along Q_3 (after Ranfagni, Ref. 9).

less and less in the A_T band and more in the A_X (lower-energy) band. At sufficiently elevated temperatures (depending again on the particular system), the emission occurs only from the X minima, having thermally escaped the T^* minimum. This model for the temperature dependence of the relative A_X and A_T emission intensities was originally proposed by Fukuda[7] and describes the phenomena in KI : Ga, KBr : Ga, KCl : Ga, NaCl : Ga, KI : In, KI : Tl, KI : Sn, KBr : Sn, and KCl : Sn. Some phosphors (KCl : Tl, KCl : In, NaCl : In) show only the A_T emission in the temperature range 4.2–300 K.

An analytical description of the thermal barrier height or the doublet energy separation $A_T - A_X$ is not available in terms of the basic parameters of the system. Lacking an analytical description, one might try to establish trends. Ranfagni *et al.*[11] give cross sections of the type shown in Fig. 1, in the framework of the linear JTE, for various values of the dimensionless product gA.[14] These curves show that $A_T - A_X$ decreases, and the barrier height increases, with a decrease of the product gA. In order to have the T^* minimum below the excitation point they find that gA must be less than 1.5. This limit implies that the curvature of the excited state is much less than that of the ground state, a result qualitatively in agreement with the results of high-pressure experiments given in paper I.

At first thought, one would expect that hydrostatic pressure would not influence a Jahn-Teller-split state. As pressure couples to the totally symmetric coordinate, it should not enhance or diminish the energy separation of the Jahn-Teller–split states, since this splitting depends on the interaction with non-totally-symmetric modes. However, hydrostatic pressure is likely to affect the basic parameters contained in gA and thereby affect the Jahn-Teller splitting. The product gA may be written

$$gA = 12G(1-\beta)/b^2 = 12GR/b^2 . \qquad (1)$$

An explicit knowledge of the pressure dependences of G, R, and b^2 is required to predict the effect of pressure on gA. Even then, the dependence of the measured transition energies and band intensities on gA is not known explicitly and can only be inferred by graphical techniques from models which have restricted use because of the number of approximations and assumptions involved.

RESULTS

The effects of high quasihydrostatic pressure on the luminescence from KI : Tl-type phosphors excited in the A band were measured at room temperature. The data presented here are from a few representative systems in which Jahn-Teller interactions perturb the excited state, as shown by the existence of an emission doublet.

To observe whether the possible effects of shear (in the high-pressure solid-state cell) on the materials were important, the luminescence from these systems was observed to 10 kbars in the hydrostatic pressure cell, using liquid hexane as the pressure fluid. No significant differences were observed in the data obtained using the solid-state or liquid cells.

The results reported here are for A-band excitation exclusively. No differences in relative emission intensities of the doublet peaks were observed while varying the excitation energy over the A band. In some materials, notably the In^+-doped potassium halides, the C band was also experimentally accessible and was observed to excite luminescence spectra identical to that from A excitation.

The In^+-doped potassium halides show several features typical of pressure-induced changes in the Jahn-Teller–split emission spectra. The material KI : In is described as an example.

At room temperature and 1 atm the emission from KI : In is dominated by the low-energy A_X band near 17 000 cm^{-1}. The emission spectra for KI : In in the low-pressure NaCl structure are shown in Fig. 2 for several pressures. The spectra in this figure have been computer corrected, normalized, and resolved. As pressure is increased above 1/atm, it is observed that the A_X band diminishes in relative intensity as a new emission begins to appear at high energy. From the low-temperature data,[7] it is found that this

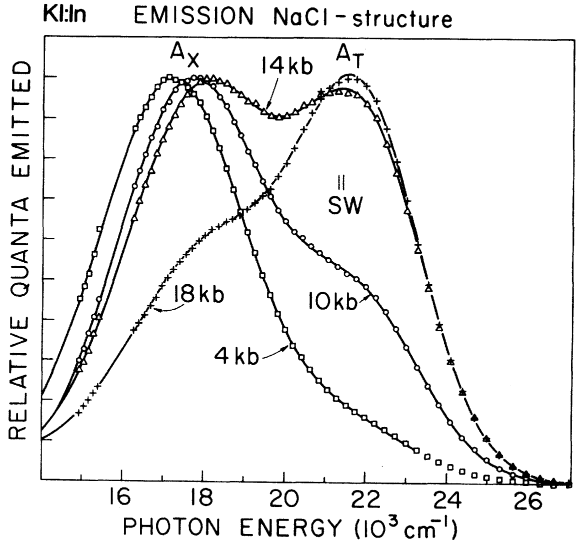

FIG. 2. Corrected emission spectra for KI: In excited in the A band at several pressures for the NaCl structure.

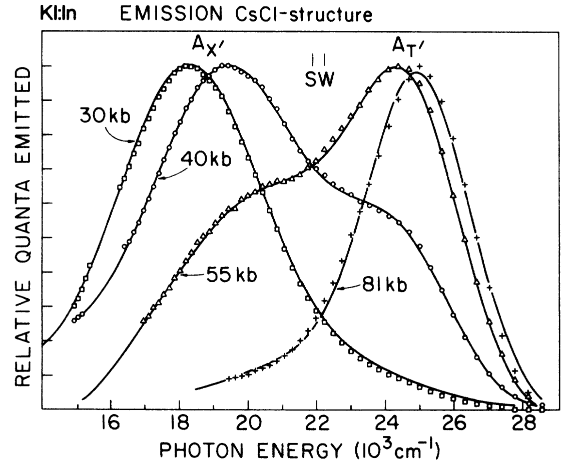

FIG. 3. Corrected emission spectra for KI: In excited in the A band for several pressures for the CsCl structure.

high-energy emission band is in fact the A_T emission seen at low temperatures. As pressure is increased, the bands shift in energy and undergo a redistribution of emission intensity within the doublet. These results also obtain in the liquid cell with purely hydrostatic pressure.

Near 19 kbars, the potassium halides undergo a phase change to the CsCl structure. For this phase, the emission spectra are shown in Fig. 3 for several pressures. These spectra exhibit a similar behavior with pressure. By 80 kbars in KI : In, the emission is dominated by the high-energy band. By analogy with the peak assignments in the NaCl phase, we have named the low- and high-energy emission bands $A_{X'}$ and $A_{T'}$, respectively, in the CsCl structure.

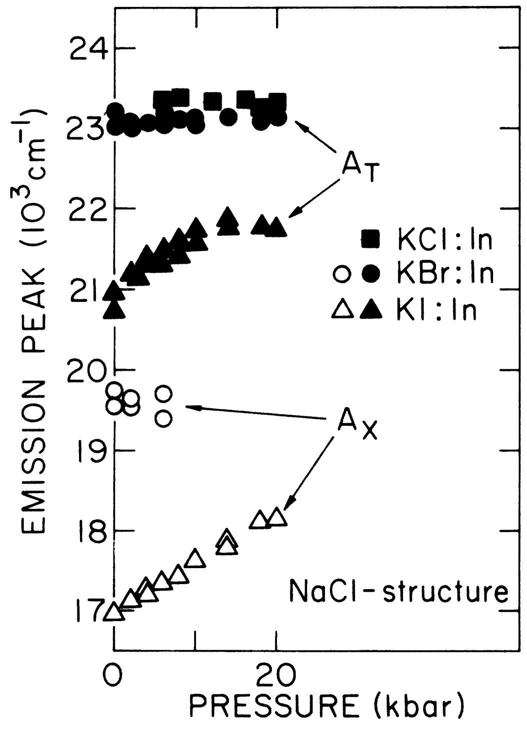

FIG. 4. Shifts with pressure of the emission bands in In$^+$-doped alkali halides in the NaCl structure.

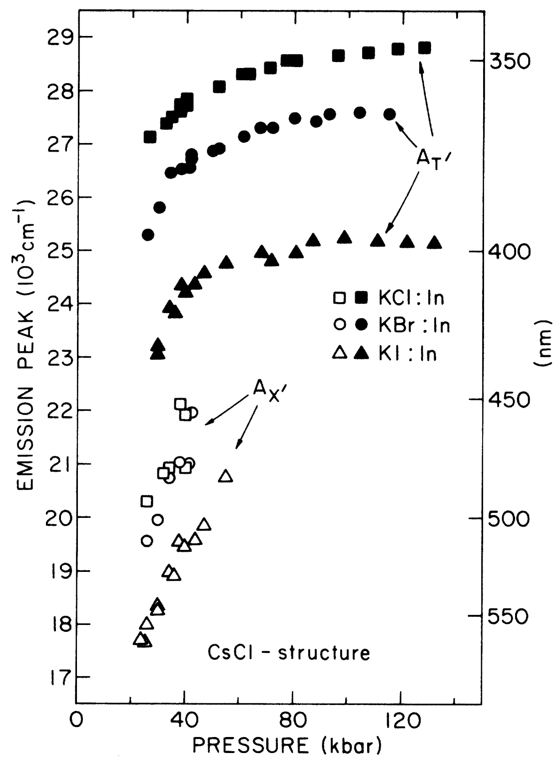

FIG. 5. Shifts with pressure of the emission bands in In$^+$-doped potassium halides in the CsCl structure.

The shifts of the emission bands with pressure for the NaCl structure are shown in Fig. 4 for the In$^+$-doped potassium halides. These shifts are characteristic of the A_X and A_T emissions; generally, a moderate blue shift (to higher energy) is observed. In KI : In, the emissions shift to higher energy almost in parallel, with a slight but significant decrease in separation which is discussed below. The large blue shift indicates that the emission excited states have a larger displacement than the ground state along the totally symmetric "breathing-mode" coordinate Q_1 (see paper I). Distortions along Q_1 should not induce any further Jahn-Teller splitting so that, as a first approximation, the bands shift parallel with pressure. The changes of half-width with pressure were found to be negligible for the A_X and A_T bands, for the most part.

The shifts with pressure of the emissions in the CsCl structure are shown in Fig. 5. Again, where

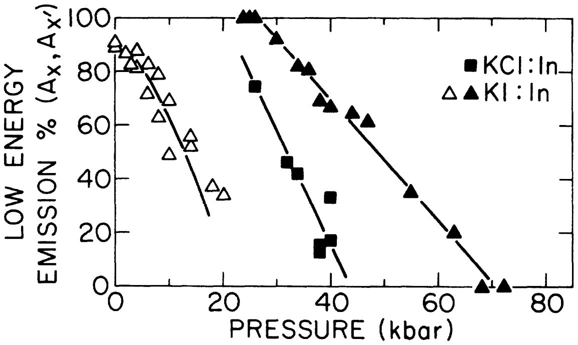

FIG. 6. Percent low-energy emission (A_X or $A_{X'}$) vs pressure for KCl: In and KI: In.

both $A_{X'}$ and $A_{T'}$ peaks are present, the shifts are roughly parallel. Based on the relative locations and the observed shifts with pressure, one can conclude that the single band in the CsCl structure of KCl : Tl is indeed the $A_{T'}$ band. It is this $A_{T'}$ band which decreases in half-width strongly with pressure, as discussed in the previous paper. The pressure changes of the $A_{X'}$-band half-width were found to be negligible.

From the computer resolutions of the doublets, one finds the relative amounts of each emission band, or the relative band intensities, from the area under the peaks. The percent emission which occurs in the low-energy A_X or $A_{X'}$ band is shown in Fig. 6 as a function of pressure for two representative phosphors. A general result for KI : Tl-type phosphors is that pressure causes a redistribution of intensity within the Jahn-Teller–induced doublet, with higher pressure favoring the higher-energy emissions. The room-temperature conversion from A_X (or $A_{X'}$) to A_T (or $A_{T'}$) depends on the impurity ion, the host lattice, and the pressure.

Similar effects of pressure on the Jahn-Teller-split luminescence are observed in a number of a alkali-halide systems; the effect is by no means of limited scope. It should be noted that, for all materials in which a pressure-induced conversion from one Jahn-Teller emission band to another was observed, the effect was reversible with pressure.

We next examine the extent of the phenomenon for those alkali halides with the NaCl structure. Figure 7 shows the A_X and A_T blue shifts for KI : Tl in the NaCl structure, as well as the relative amount of the low-energy emission. The Tl^+-doped system behaves similarly to the In^+-doped material. In KBr : Tl, the A_X-to-A_T conversion is complete by 12 kbars with about 50% of the total emission in each band at 0 kbar. For KCl : Tl, no A_X was observed at any pressure; this is consistent with Fukuda's assignment that the KCl : Tl emission is the A_T band.

For both sodium and potassium halides, the amount of A_X at zero pressure increases in the order chloride, bromide, iodide. No A_X is seen in NaCl : Tl at any pressure. In NaBr : Tl, a small amount of A_X (<5%) exists at zero pressure; by 2–3 kbars, only A_T exists. The A_X emission in NaI : Tl comprises about 90% of the zero-pressure emission. As pressure is increased, the A_X emission decreases, but levels off near 50% by 60 kbars; this percentage remains to 140 kbars. The lack of complete conversion in this system may be due to the turnaround of the A_T emission shift at high pressure (40–60 kbars) in the NaCl structure; as discussed later, the conversions can be related to the peak shifts. A similar result holds for NaI : In; the pressure-induced conversion A_X to A_T was not completed in the pressure range studied.

The A_T emission in NaI : Tl initially shifts blue, then reverses and shifts red. This shift is characteristic of the A_T band and identifies the band in NaCl : Tl (where only a single band exists) as the A_T emission.

Table I summarizes the room-temperature loca-

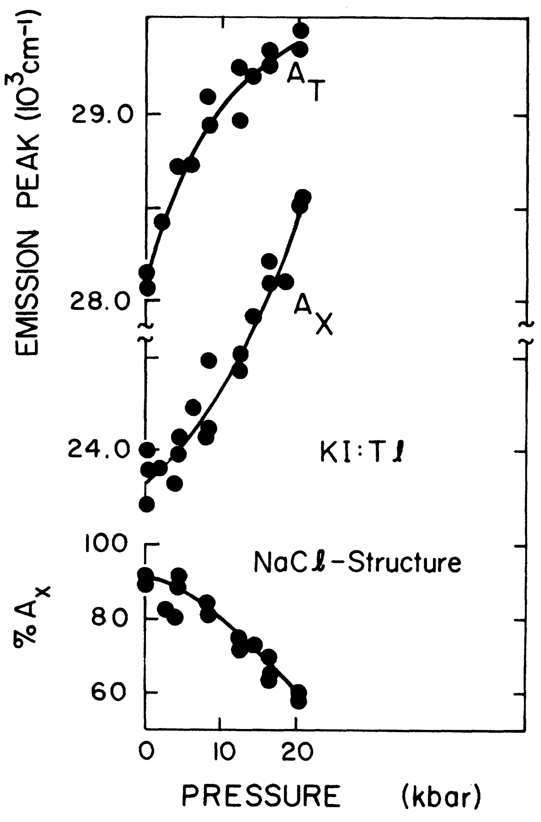

FIG. 7. Emission band shifts and percent low-energy (A_X) emission for KI: Tl in the NaCl structure.

TABLE I. Locations of A_X and A_T emission bands in systems with the NaCl structure. At room temperature, excited in A band. All energies in 10^3 cm^{-1}.

	1 atm		High pressure			
System	A_X	A_T	P	A_X	A_T	%A_X
NaCl: Tl	...	34.1	a			
NaBr: Tl	...	32.3	a			
NaI: Tl	23.2	29.3	60	≈ 26.8	29.4	50
KCl: Tl	...	32.8	a			
KBr: Tl	27.7	31.7	0	27.7	31.7	50
KI: Tl	23.85	28.15	10	24.35	29.05	80
NaCl: In	...	23.8	a			
KCl: In	...	23.3	a			
KBr: In	19.6	23.1	0	19.6	23.1	30
KI: In	17.0	20.9	13	17.8	21.8	50
KCl: Ga	18.8	...	18	19.2	23.7	≈ 80
KI: Ga	15.9	...	a			

[a] Conversion from A_X to A_T is not seen in the pressure range studied.

TABLE II. Locations of $A_{X'}$ and $A_{T'}$ emission bands in systems with the CsCl structure. At room temperature, excited in the A band. All energies in 10^3 cm^{-1}.

	1 atm		High pressure			
System	$A_{X'}$	$A_{T'}$	P	$A_{X'}$	$A_{T'}$	%$A_{X'}$
KCl: Tl	...	...	25	...	36.75	0
KBr: Tl	...	...	25	...	34.6	0
KI: Tl	...	...	25	...	31.0	0
NH_4Cl: Tl	25.8	...	18	29.0	36.5	50
CsBr: Tl	27.6	...	32	32.7	35.2	50
RbI: Tl	...	...	20	24.8	31.7	50
KCl: In	...	...	32	20.8	27.4	50
KBr: In	...	...	35	20.4	26.4	50
KI: In	...	...	50	20.3	24.7	50
CsBr: In	19.0	...	60	24.5	26.5	50
CsI: In	17.6	...	90	22.7	25.3	50
KCl: Ga	...	...	95	22.0	26.8	~ 50
KI: Ga	...	...	30	16.5	...	100[a]

[a] Does not convert from $A_{X'}$ to $A_{T'}$ at pressures below 130 kbars.

tions of the A_X and A_T emissions observed in materials with the NaCl structure. The band locations are given at 1 atm and at some particular elevated pressure and conversion percentage.

It has been indicated above that similar emission bands are observed in CsCl-structure materials. The In$^+$-doped potassium halides display a doublet structure in the high-pressure CsCl-phase emission spectra; these peaks were assigned the nomenclature $A_{X'}$ and $A_{T'}$, by analogy to the NaCl structure.

For the Tl$^+$-doped potassium halides in the CsCl phase, no $A_{X'}$ bands are observed. The emission is denoted $A_{T'}$, as determined from the effect of pressure on the band and by analogy with the In$^+$-doped potassium halides. The emission from the system NH_4Cl: Tl was also observed to high pressure. This material displays the CsCl crystal structure as well. The low-pressure emission ($A_{X'}$) occurs near 25 800 cm^{-1} when excited near 250 nm. This emission shifts blue rapidly and, between 15 and 25 kbars, converts completely to a high-energy emission band ($A_{T'}$) near 37 500 cm^{-1}. Similarly, in CsBr : Tl, the $A_{X'}$ band shifts blue strongly at low pressures. Near 20 kbars, the $A_{X'}$ begins to disappear continuously as the $A_{T'}$ band grows in. The conversion is completed by 40 kbars, and the $A_{T'}$ band characteristically shifts blue, turns around at very high pressure, and narrows dramatically. The same phenomena are observed in CsBr : In and CsI : In; the percentage of the $A_{X'}$ emission vs pressure for these three materials is shown in Fig. 8. Similar behavior was observed in the CsCl phase (above 5 kbars) of RbI : Tl. By 24 kbars, the single $A_{T'}$ emission is present in this material.

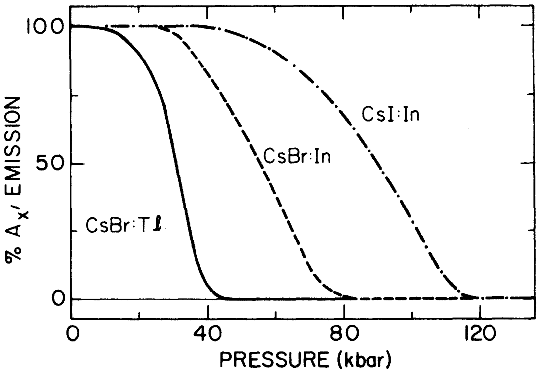

FIG. 8. Percent low-energy emissions ($A_{X'}$) vs pressure for CsBr: Tl, CsBr: In, and CsI: In.

Table II summarizes the $A_{X'}$- and $A_{T'}$-emission-band locations observed in CsCl-structure crystals at room temperature. Where available, the 1-atm values are given in the left columns. On the right, the $A_{X'}$ and $A_{T'}$ energies are given for a particular pressure and conversion percentage.

The results of high-pressure emission studies on CsI : Tl have been deferred until now. This system has a complex pressure behavior yet is in many ways similar to the phosphors discussed above. At room temperature and zero pressure, the A-band excitation leads to a single emission at 17 400 cm^{-1}. As the pressure is increased, this band (labeled E_1) shifts blue; a new emission band (E_2) grows in at higher energy (near 26 000 cm^{-1}), which also shifts blue. By 30 kbars, the E_1 band has essentially disappeared; meanwhile, a third emission (E_3) has begun to grow in at still higher energy (near 32 000 cm^{-1}). Near 50 kbars, the E_3 band becomes the only emission band. The shifts of these bands are given in Fig. 9, where the dashed sections of the best-fit curves represent regions where the particular emission comprises less than

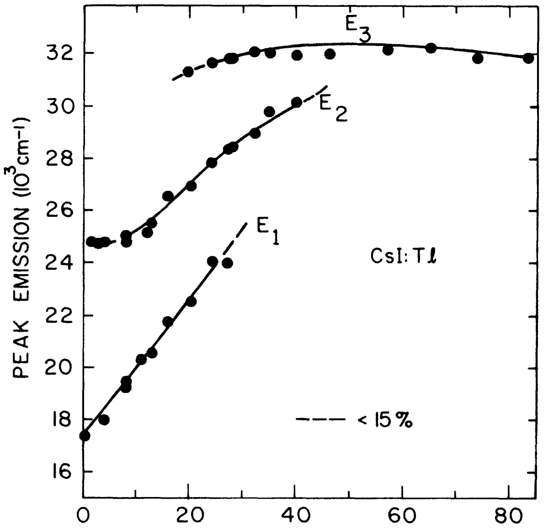

FIG. 9. Emission band shifts vs pressure for CsI: Tl.

15% of the total emitted light. The observed percentage emissions from the three bands are shown in Fig. 10. The E_3 band behaves very much like the $A_{T'}$ band in other materials; it shifts blue initially, turns around at high pressures, and narrows substantially with increasing pressure.

The phosphor CsI : Tl displays the dramatic effect which high pressure can have on electronic transitions in solids. The combined effects of emission-band shifts with pressure and conversions from one band to another cause an overall (continuous) change in emission energy of nearly 15 000 cm^{-1} (1.86 eV) in 50 kbars. This emitted light shifts from 575 nm (yellow-green) at zero pressure, through much of the visible spectrum, to 310 nm in the near uv by 50 kbars.

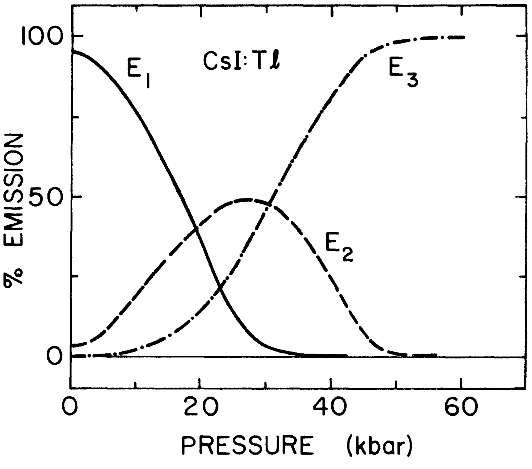

FIG. 10. Percentage of total emission due to each of the three emission bands vs pressure in CsI: Tl.

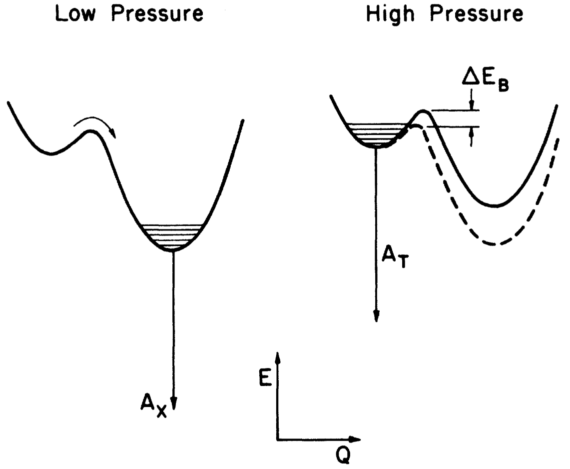

FIG. 11. Cross sections of $^3T_{1u}$ APES along the reaction coordinate $A_X \rightarrow A_T$ at low and high pressures. The dashed curve at high pressure represents the low-pressure situation.

DISCUSSION

We propose a model, consistent with the known coexistence of two types of minima on the excited-state $^3T_{1u}$ APES, which describes the effect of pressure on the Jahn-Teller-split luminescence from KI : Tl-type phosphors.

Figure 11 shows the structure of a cross section of the excited-state APES along some coordinate Q, which suitably describes the thermal-relaxation path. At room temperature and low pressure, the emission is predominantly A_X, having thermally escaped the higher-energy T minimum. As pressure is increased, we propose that the thermal barrier increases by an amount ΔE_B, depending on the pressure, leading to more A_T and less A_X emission. At some elevated pressure, then, only A_T emission can occur. This describes the results obtained in most systems where the pressure-induced A_X-to-A_T conversion is exhibited. As pressure is increased, the tetragonal Jahn-Teller state is preferred over the rhombic state.

Next, we make the assumption that the change in ΔE_B is due to the relative vertical displacement between harmonic wells which describe the T and X minima along Q. As a zeroth-order approximation, the barrier increase ΔE_B is approximately equivalent to the decrease in energy separation between the well minima. Certainly this approximation can only give a qualitative description of the phenomena, as it assumes that the force constants of the wells are independent of pressure and that the horizontal separation of the minima is independent of pressure. The energy separation between the T and X minima can be directly

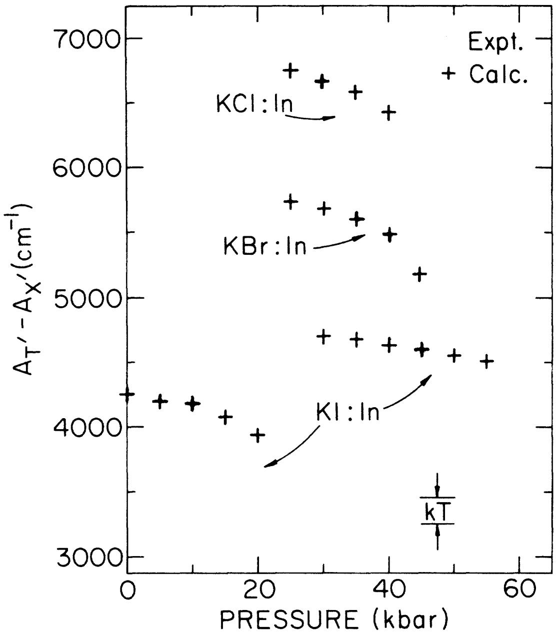

FIG. 12. Comparison of experimental and calculated values for the emission doublet energy separation vs pressure. The calculated values are obtained from observed intensity changes with pressure.

measured as the emission doublet energy separation, $A_T - A_X$. The probability of thermal escape from the T minimum at one pressure relative to that at another can then be determined from a Boltzmann factor involving the change in barrier height. The probability of thermal escape from the T minimum is also proportional to the probability that an A_X emission occurs. One can then quantitatively relate the observed A_X emission intensity (percentage) to the observed emission doublet separation.

In practice, one takes the ratio of the A_X-emission percentages at two pressures and calculates the change in barrier height ΔE_B which causes this intensity change. One then assumes a value for $A_T - A_X$ at one pressure and calculates $A_T - A_X$ at other pressures. These calculated values can be compared to the experimental value.

This comparison is shown in Fig. 12 for the In$^+$-doped potassium halides which exhibit conversion of the type $A_X \rightarrow A_T$ or $A_{X'} \rightarrow A_{T'}$ with pressure. The shaded regions show the experimentally observed emission doublet energy separations vs pressure. These values represent differences of smooth curves through the peak shifts for $A_{T'}$ (A_T) and $A_{X'}$ (A_X) bands. Though some uncertainty in the energy separation results, it is certain that the $A_{T'}$ (or A_T) and $A_{X'}$ (or A_X) bands shift slightly differently with pressure, with their separation decreasing. From the observed changes in A_X or $A_{X'}$ intensity with pressure, as shown in Fig. 6, the expected changes in $A_T - A_X$ or $A_{T'} - A_{X'}$ can be found using the above model. These calculations yield the plusses in Fig. 12. (The calculated values for each compound are vertically adjusted to match $A_T - A_X$ or $A_{T'} - A_{X'}$ at one pressure.) The agreement is quite good, considering the simplicity of the model. It should be noted that the different rates of conversion with pressure in different potassium halides are reflected in the corresponding rates of change of $A_{T'} - A_{X'}$ with pressure. The conversion was seen to be slower in KI than in KCl, as shown in Fig. 6; correspondingly, $A_{T'} - A_{X'}$ decreases less in KI than in KCl over a given pressure interval.

The calculated values in Fig. 12 systematically have less slope than the experimental values. This means that, as calculated from the emission intensity changes, the thermal barrier energy increases less with pressure than the energy separation of the well minima decreases. A careful inspection of the wells in Fig. 11 predicts the same.

In terms of the basic parameters, it is apparent that the product gA decreases with pressure. It has been shown earlier that R is relatively insensitive to modest pressure changes, and one would expect the exchange integral G to change very little with pressure, since it relates basically only to the impurity ion. From (1), one can conclude that gA decreases with pressure because of an increase with pressure in b, the electron-lattice coupling parameter to tetragonal vibrations. It is well known that pressure strongly affects the overlap of adjacent orbitals. As pressure is increased, the overlap between p_x orbitals of the impurity ion and the neighboring anion orbitals should increase, thereby increasing b^2. Using a point-charge model, Toyozawa and Inoue[4] derived an expression for b^2; it is, for monovalent impurities,

$$b^2 = \frac{18}{50} \frac{e^4 \langle r^2 \rangle^2}{\gamma^2 d^9 (c_{11} - c_{12})}, \tag{2}$$

where $\langle r^2 \rangle$ depends only on the impurity ion, γ is a constant on the order of 1, d is the nearest-neighbor separation in the lattice, and c_{11} and c_{12} are elastic constants. As far as pressure effects are concerned, one would expect the strong dependence of b on d to dominate, so that one obtains, using (1) and (2),

$$gA \sim GRd^9. \tag{3}$$

Hence, since increasing pressure decreases d, gA should decrease with pressure. (For example, for KBr in the CsCl structure, d^{-9} increases by approximately 35% between 20 and 70 kbars.)

This explains the observed effect of the $A_X \rightarrow A_T$ and $A_{X'} \rightarrow A_{T'}$ conversions.

The similarities in emission spectra and their behavior with pressure for materials in the CsCl structure and the NaCl structure indicate a similarity in the nature of their excited states. Very little theoretical or experimental attention has been given to the role of the JTE in the luminescence from phosphors with the CsCl structure. Since this structure is also cubic, the same lattice distortions Q_i are available for both CsCl and NaCl structures, and the Jahn-Teller effect should be operable.[15] In addition, the large spin-orbit coupling in the cesium halides leads one to suspect that emission structure in the CsBr : Tl-type phosphors is caused by the same types of minima on the ${}^3T_{1u}$ APES as in KI : Tl-type phosphors. Zazubovich[16] presents one of the few optical studies of CsBr : Tl-type phosphors. He observed, at 90 K, two emissions from CsBr : In and CsI: In which are located very close to the $A_{X'}$ and $A_{T'}$ bands seen at room temperature and high pressure. From polarization studies he concludes that the emitting centers in CsBr : Tl-type phosphors have tetragonal sysmmetry. This result further indicates the presence of the JTE and that the $A_{X'}$ and $A_{T'}$ bands are closely related to the A_X and A_T bands found in phosphors with the NaCl-structure.

Several trends have been observed for the $A_T - A_X$ and $A_{T'} - A_{X'}$ emission doublet energy separations. In the NaCl structure, the separation $A_T - A_X$ increases with the anion series $Br^- \rightarrow I^-$, decreases along the cation series $Na^+ \rightarrow K^+$, and increases with the metal-ion series $In^+ \rightarrow Tl^+$. For phosphors with the CsCl structure, $A_{T'} - A_{X'}$ increases with the metal-ion series $Ga^+ \rightarrow In^+ \rightarrow Tl^+$ and decreases with the cation series $K^+ \rightarrow Cs^+$. For the potassium halides in the CsCl structure, the anion series $Cl^- \rightarrow Br^- \rightarrow I^-$ gives a decrease in doublet separation, while the same series appears to give an increase for the cesium halides.

The pressures necessary for the onset of $A_X \rightarrow A_T$ or $A_{X'} \rightarrow A_{T'}$ conversion changes with the material. Generally speaking, the necessary pressure increases in the series $Na^+ \rightarrow K^+ \rightarrow Cs^+$ and $Cl^- \rightarrow Br^- \rightarrow I^-$, and decreases in the series $Ga^+ \rightarrow In^+ \rightarrow Tl^+$. Thus, in KI : Ga, 130 kbars is insufficient to cause the conversion $A_{X'} \rightarrow A_{T'}$; for KI : In, this conversion occurs near 40 kbars, and in KCl : In, the conversion is completed at some pressure below the phase transition. For KCl : Tl, only the A_T band is ever seen, while in KI : Tl, a pressure above 20 kbar would be necessary (were it not for the phase transition) to complete the $A_X \rightarrow A_T$ conversion.

The pressure range necessary for completion of the conversion increases in the series $Cl^- \rightarrow Br^- \rightarrow I^-$. This describes the rate (with pressure) of the conversion.

We conclude this section with a discussion of CsI : Tl, in which three different emission bands were observed at room temperature. As pressure increases, the bands convert as $E_1 \rightarrow E_2 \rightarrow E_3$, in order of increasing energy. Based on the subsequent pressure behavior of the E_3 band, this emission is probably the $A_{T'}$ band. From the shifts in Fig. 9, it is clear that the energy separations $E_2 - E_1$ and $E_3 - E_2$ decrease with increasing pressure. The direction of conversion (that high pressure favors high-energy emissions) indicates that, at least qualitatively, the excited states in CsI : Tl behave like those in KI : Tl-type phosphors, only now three minima coexist, rather than two. As pressure increases, the separation $E_2 - E_1$ decreases, which raises the barrier height between states 1 and 2 and causes the disappearance of the E_1 emission. Further increases in pressure diminish $E_3 - E_2$ which raises the barrier between states 2 and 3, leaving only E_3 emission.

Zazubovich[16] pointed out an interestingly anomalous result for CsI : Tl. He observed, from low-temperature polarization studies, that the emitting center in CsI : Tl has trigonal symmetry, instead of the tetragonal symmetry found for other phosphors. He suggests that this is caused by the strength of the $I^- - Tl^+$ covalent bond; if this bonding is strong enough, the π-like bond in the excited state will be directed from the Tl^+ to the I^- along the body diagonal of the cubic cell. This direction has trigonal C_3 symmetry. The zero-pressure emission E_1 is thus from a state of trigonal symmetry. This suggests that E_2 is the analog to the $A_{X'}$ band in other KI : Tl-type phosphors and may be from a state of rhombic symmetry. That these assignments may be correct is substantiated by the recent work of Bacci, Ranfagni, Fontana, and Viliani.[13] They treat the quadratic JTE for a triply degenerate electronic term in an O_h complex with both E_g and T_{2g} modes and find that tetragonal minima can coexist with orthorhombic or trigonal minima. More importantly, they mention briefly that, for particular values of the relevant parameters, the coexistence of all three types of minima—tetragonal, orthorhombic, and trigonal—is possible. This is apparently the case for CsI : Tl.

In summary, the doublet emission from KI : Tl-type phosphors is strongly affected by the application of high hydrostatic pressures. In general, pressure causes a redistribution of intensity within the doublet, with high pressure favoring the high-energy emissions from states of tetragonal symmetry. A pressure model of the excited Jahn-Teller–split state describes this redistribution in terms of the observed emission-band shifts with pressure. The pressure-induced conversion of the emission from a rhombic symmetry state to emission from a tetragonal symmetry state is found to be a general phenomena which occurs in many doped alkali halides, in both NaCl and CsCl crystal structures. In CsI: Tl, three different emission bands were observed at different pressures; these bands correspond to emission from states of trigonal, rhombic, and tetragonal symmetry.

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