PHYSICAL REVIEW B VOLUME 31, NUMBER 8 15 APRIL 1985

Optical spectroscopy of Pb^{2+} in NaCl: Validity of a Jahn-Teller (Fukuda) model

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(Received 12 July 1984)

The optical spectroscopy (luminescence and decay-time measurements) of Pb^{2+} in doubly doped NaCl:M^{2+},Pb^{2+} (M=Mg, Ca, Sr, Pb) has been studied. Two emission bands have been observed, one of them appearing at 310 nm in all systems whereas the position of the other band (at about 380 nm) is affected by the additional ion M^{2+}. These results have been interpreted in terms of a Jahn-Teller model which considers two kinds of minima in the adiabatic potential-energy surface (APES). The role of the M^{2+} ion in the Pb^{2+}APES is discussed.

I. INTRODUCTION

The optical spectroscopy of monovalent ns^2 ions (Tl^+, In^+, Ga^+) in alkali halides has been extensively studied. The luminescence properties are particularly interesting, since they show a rather complex behavior, which is markedly dependent on the host-impurity system.[1] However, in spite of the variety of the reported results, most features of the luminescence spectra can be understood in terms of a model, initially developed by Fukuda,[2] that takes into account the possibility of several nonequivalent minima in the adiabatic potential-energy surface (APES) of the excited levels, induced by the combined effect of spin-orbit splitting and electron-lattice interaction. Later on, a number of detailed calculations[3-6] including linear as well as quadratic Jahn-Teller coupling terms, have been reported which provide a more quantitative basis for that model. These calculations have confirmed the possible coexistence of tetragonal and lower symmetry minima in the APES or the existence of only one of such types of minima, depending on the relative values of the various contributions to the impurity-lattice Hamiltonian.

The situation for divalent ns^2 cations, such as Sn^{2+} and Pb^{2+} is much less satisfactory, particularly, for the latter ion. One main reason is that the presence of charge-neutralizing vacancies provides the impurity with a high diffusivity and consequently very efficient aggregation and precipitation processes take place even at very low concentrations (≤ 100 ppm). Although the changes in the absorption and luminescence spectra of Pb^{2+} have proved to be very useful in following those clustering processes[7,8] they have obscured the study of the spectroscopy of isolated Pb^{2+}-vacancy dipoles. On the other hand, even for isolated dipoles, the impurity is subjected to a crystal field of reduced (less than cubic) symmetry that should influence the optical behavior. This situation is at variance with the case for monovalent ions where a cubic field is generally assured.

One example of the situation found for the divalent ns^2 cations, is provided by Pb^{2+} in NaCl. For excitation at the A (and C) band, two emission bands are observed at 310 and 380 nm, which relative intensity very critically depends on the impurity concentration and previous thermal treatments.[9] Since the 380-nm band grows during annealing at the cost of the 310-nm emission, it has been often attributed to emission from lead aggregates (e.g., trimers) whereas the 310-nm band has been associated to isolated dipoles.[10,11]

Marculescu[12] and more specifically Pascual *et al.*,[9] after a detailed study of the optical spectra under a variety of treatments, suggested that the two emissions should derive from two minima in the APES, in a similar way to the case of monovalent ions. The proposal that the 380-nm emission cannot be solely associated to a definite Pb^{2+} cluster has very recently found a solid support, when experiments on NaCl samples doped with Pb^{2+} together with another divalent cation M^{2+} have been performed.[13] It has been shown that essentially the same two emissions at 310 and 380 nm are observed whichever the impurity M^{2+} (M=Mg, Ca Sr, Ba).

The purpose of this work has been to provide additional experimental evidence to support the Fukuda model for the case of Pb^{2+} in NaCl. In particular, lifetime measurements have been performed that fit into such a scheme and allow for a qualitative understanding of the structure of the APES for the $^3T_{1u}$ levels. The experiments have been performed on singly Pb^{2+} as well as Pb^{2+}-M^{2+})-doped NaCl.

II. EXPERIMENTAL

NaCl single crystals doped with a small (~ 10 ppm) concentration of lead together with a much higher concentration of another M^{2+} cation have been grown in our laboratory by the Czochralski method in argon atmosphere. Some other crystals exclusively doped with lead at a higher concentration were also grown by the same procedure. Table I provides a list of systems and concentrations used in this work. Concentrations have been measured in the crystal by atomic absorption spectropho-

TABLE I. NaCl:Pb^{2+},M^{2+} doubly doped systems used in this work.

M^{2+}	$C_{M^{2+}}$ (ppm)	$C_{Pb^{2+}}$ (ppm)
Mg	200	8
Ca	1282	4
Sr	346	11
Pb		25

tometry except for magnesium where it was estimated from that in the melt through the known segregation coefficient.

Luminescence (excitation and emission) spectra were measured with a Jobin-Yvon model no. JY-3CS spectrofluorimeter with capability of spectra accumulation and obtaining successive derivatives. Temperature variation in the range 11–320 K was achieved with a closed-cycle helium cryostat.

Decay-time measurements were performed under flash-lamp broadband excitation and using monochromator or suitable optical filters to select A_T or A_X emission. The samples were annealed at 500 °C for $\frac{1}{2}$ h and luminescence measurements were taken within a few minutes after quenching to RT.

III. RESULTS

A. Emission bands in Pb^{2+} and Pb^{2+}-M^{2+} doped NaCl

In accordance with previous work,[8,9,11] excitation at the A band of Pb^{2+} in well-quenched NaCl:Pb crystals yields, for all cases, two fluorescence bands at 310 (A_T emission) and 380 nm (A_X emission). The relative intensity of the two emissions critically depends on the state of aggregation of the impurity, i.e., on lead concentration and thermal history of the sample.[9] In particular, for low-doped and well-quenched samples the intensity I_X of the A_X band is hardly detectable.

For crystals, which have been doped with a divalent cation impurity M^{2+} (Sr^{2+}, Ca^{2+}, etc.) in addition to Pb^{2+}, it has been very recently shown[13] that essentially the same two emissions at 310 and 380 nm are observed. However, the ratio I_X/I_T is markedly enhanced with regard to crystals solely doped with the same concentration of Pb^{2+}. This has been considered as an evidence that the two emissions are characteristic of Pb^{2+} ions, the relative emission yield being altered when a M^{2+} ion sits close to the emitting lead ion forming a mixed Pb^{2+}-M^{2+} dimer (or slightly larger aggregates). In order to ascertain whether the presence of the close-by M^{2+} ions may slightly influence the Pb^{2+} spectra, the precise location of the A_T and A_X emission band peaks has been determined for various additional M^{2+} dopants. Figure 1 shows the peak position of the A_T and A_X emission bands at 11 K as a function of the ionic radius of the codopant impurity. The position of the A_T band remains constant whereas the A_X emission presents a variation in its position of 8 nm as one moves from Mg^{2+} to Pb^{2+}. Moreover, the effect of temperature has been carefully investigated in order to detect any shift or splitting of the band. The A_T band peak shows, as expected, a continuous evolution towards longer wavelength when heating the sample from 10 to 300 K. No sign of splitting has been detected. On the other hand, the A_X band peak shows slight but abrupt change in wavelength at a given temperature T_Δ. Illustrative data are shown in Fig. 2 for NaCl:Pb^{2+},Mg^{2+}, where the jump ΔE in the energy of the peak occurring at $T=60$ K has been marked.

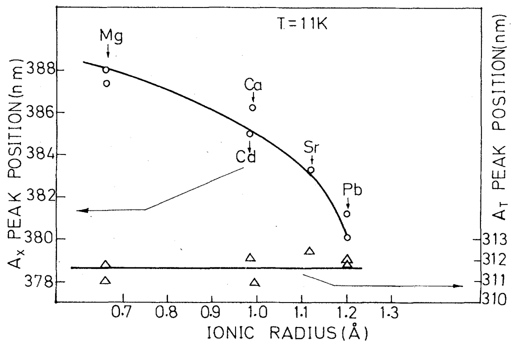

FIG. 1. Peak position of the A_T and A_X emission bands at 11 K as a function of the ionic radius of the codopant impurity.

The values of ΔE for various systems are listed in Table II. The abrupt change in the energy of the A_X transition suggests that two different and close Pb^{2+} levels may be involved at low ($T<T_\Delta$) and high ($T>T_\Delta$) temperatures. A reasonable possibility is that the two close levels correspond to an A_X minimum in one of the split branches of the ${}^3T_{1u}$ APES and to a reservoir ${}^3A_{1u}$ level lying behind it.[6] Additional data will now be presented to test this idea.

B. Excitation spectra

The excitation spectra corresponding to the two A_T and A_X emissions have been determined for all doped systems used in this work. Although both excitations lie at the same A spectral region there are clear and systematic differences between them. In fact, the excitation for the A_X emission always occurs at higher energies than that corresponding to the A_T emission as can be seen in Fig. 3 where both excitation bands have been normalized to the maximum intensity. On the other hand, by using second-

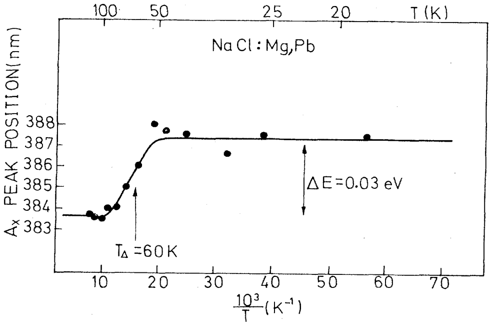

FIG. 2. Temperature dependence of the peak position of the A_X emission band in NaCl:Mg^{2+},Pb^{2+}.

TABLE II. A_X emission peak shifts (ΔE) and onset of decreasing A_X lifetime (E_s).

	Mg,Pb	Ca,Pb	Sr,Pb	Pb,Pb
ΔE (eV)	0.03	0.02	0.03	0.02
E_S (eV)	0.025	0.015	0.023	0.022

derivative excitation spectroscopy, it has been possible to resolve the structure of the excitation spectra for both A_T and A_X emissions. This structure for the A_T emission has already been reported[14] for NaCl crystals exclusively doped with lead. In the case of the doubly doped crystals the behavior obtained for all studied systems is similar and can be illustrated with the data (77 K) corresponding to NaCl:Pb,Mg shown in Fig. 4(a). Both excitation bands present a clear splitting in doublets more pronounced for the A_X excitation band. Moreover, it has been carefully checked that the amount of splitting grows linearly with the square root of the absolute temperature, as plotted in Fig. 4(b) for the A_X excitation.

Figure 5 shows the measured peak values at 77 K for the two components of the A_X excitation, plotted as a function of the ionic radius of the M^{2+} impurity acting as a codopant of Pb^{2+}. Allowing for experimental scatter, the magnitude of the splitting appears to be essentially independent of the nature of M^{2+}. This will have some bearing on the final discussion of the luminescence processes.

C. Temperature dependence of intensity and lifetime of A_T and A_X emissions

The intensity of the two A_T and A_X emissions has been determined as a function of temperature for all doped systems. The data, which are plotted in Figs. 6(a) and 6(b) do not show any appreciable dependence on the particular system, the behavior being essentially similar for $NaCl:Pb^{2+},M^{2+}$ as for $NaCl:Pb^{2+}$ crystals. The luminescence yield keeps constant from 10 K up to $T_q = 180$—200 K where thermal quenching becomes operative. For temperatures well above T_q, an exponential decay of the luminescence intensity $I = I_0 e^{-E_q/kT}$ is observed, which allows for the determination of the effective energy barrier E_q for the quenching. E_q values for the different systems are listed in Table III.

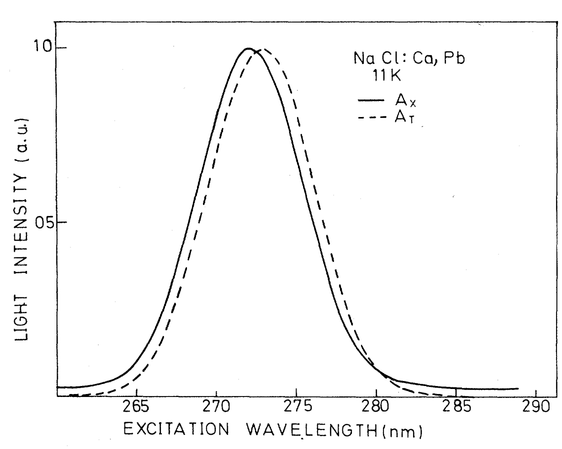

FIG. 3. Excitation spectra of the A_T and A_X emission bands in $NaCl:Ca^{2+},Pb^{2+}$.

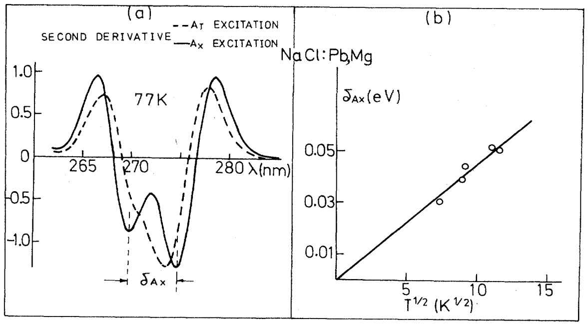

FIG. 4. Doublet structure of the A_T and A_X excitation bands (a). Temperature dependence of the splitting δ_A (b).

In order to gain additional insight into the arrangement of the excited levels of Pb^{2+}, the lifetimes of the A_T and A_X emissions have been measured as a function of temperature in the range 10—250 K. Main conclusions derived from this study are the following.

(i) The A_T emission shows (at least), two clear contributions to its decay. There is a fast component with a lifetime $\tau_F \sim 15$ ns, essentially independent of temperature and a slow lifetime τ_s markedly dependent on temperature. The results for NaCl exclusively doped with lead are essentially the same, which have already been reported.[15] As observed in previous work, the transition between the two, fast and slow, components, may suggest the presence of another component with an intermediate lifetime. However, since this component is not clearly defined, it will not be further considered. The dependence of τ_s with temperature for NaCl:Pb and NaCl:Pb:Sr is plotted in Fig. 7, showing that the behavior of doubly doped samples is quite similar although not identical to that of exclusively Pb-doped crystals.

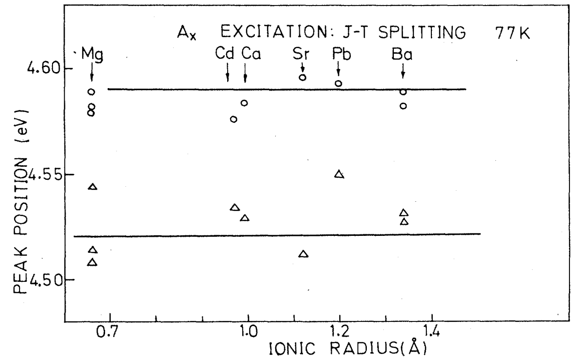

FIG. 5. Peak position of the components of the split A_X excitation as a function of the ionic radius of the codopant impurity.

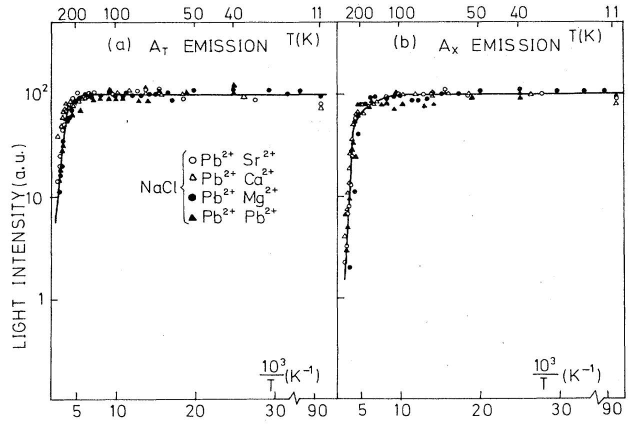

FIG. 6. Temperature dependence of the intensity of the A_T (a) and A_X (b) emission bands for different doubly doped systems.

(ii) The A_X emission shows a slow component exclusively, with a temperature-dependent lifetime τ_s. The dependence of τ_s on T is shown in Fig. 8. It is to be noted that τ_s keeps constant from 10 to 30 K and then markedly decreases on increasing T in a region where the emission yield still remains constant [see Fig. 6(b)]. For temperatures $T > 30$ K the dependence of τ_s on T becomes exponential $\tau_s = \tau_0 e^{-E_s/kT}$ from where E_s can be obtained. E_s values are listed in Table II, together with those for ΔE. E_s and ΔE are quite close to each other, suggesting that the two phenomena (A_X peak shift and onset of decreasing A_X lifetime) are closely related. The saturation values reached for the lifetime τ_s at low temperatures ($T < 30$ K) are rather long and point to a forbidden transition mechanism for the A_X luminescence.

IV. DISCUSSION

In accordance with prior data it has been recently established that the A_T emission closely correlates with the concentration of isolated Pb^{2+}-vacancy dipoles monitored by ionic thermocurrents.[16] On the other hand, the A_X emission is markedly enhanced when lead dimers (or aggregates) as well as mixed Pb^{2+}-M^{2+} dimers (or aggregates)[13] are formed. Therefore, one can conclude, as previously assumed, that the A_T band is associated to an optical transition of Pb^{2+} ions when they are in the form of isolated dipoles. However, the results described in this paper show that the A_X band, at variance with some previous proposals[10,17] do not necessarily involve Pb^{2+} clusters, but it is indeed associated to levels of Pb^{2+} in the neighborhood of another divalent cation (either Pb^{2+} or M^{2+}).

The results obtained in this work about the variation in the position of the A_T and A_X bands with the ionic radius of M^{2+} are in agreement with the above assumption. The A_T band position is independent of additional doping, in accordance with its assignment to Pb^{2+} dipoles, whereas the shift in the A_X peak position can be induced by the close-by M^{2+} ions in the Pb^{2+}-M^{2+} clusters.

The question now is to explain why the A_T emission disappears, when Pb is forming Pb^{2+}-M^{2+} aggregates and is turned into the observed A_X band.[13,16] In order to assign these two emissions to specific Pb^{2+} levels, it is plausible to think that Fukuda's model, that has been satisfactorily used to account for most monovalent ns^2 ions properties can be also applied to this situation. This suggestion has already been put forward by Pascual *et al.*[9] In fact, in alkali halides doped with monovalent ns^2 ions, the two observed emissions, A_T and A_X, have, respectively, the same symmetry as the 310- and 380-nm bands reported for Pb-doped NaCl.[11] Moreover, the energy separation is quite similar in the two cases.[9]

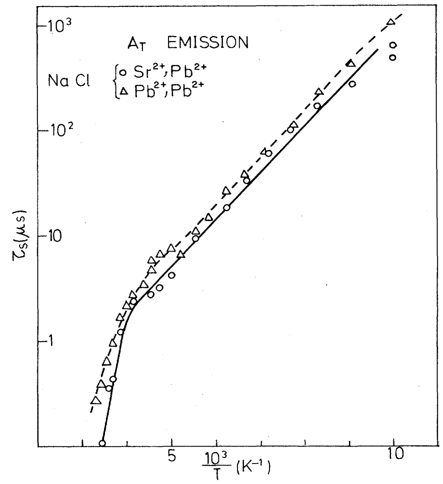

FIG. 7. Temperature dependence of the slow component, τ_s, of the A_T lifetime.

TABLE III. Effective energy barriers, E_q, for quenching.

		Mg,Pb	Ca,Pb	Sr,Pb	Pb,Pb
E_q (eV)	A_T	0.24	0.24	0.19	0.25
	A_X	0.18	0.06	0.15	0.15

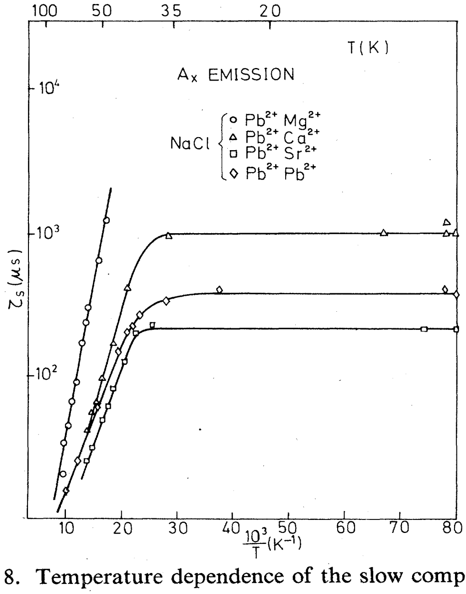

FIG. 8. Temperature dependence of the slow component, τ_s, of the A_X lifetime.

In this model, the A_T and A_X emissions have to be associated to transitions from two different minima in the APES of the ${}^3T_{1u}$ excited state to the ${}^3A_{1g}$ ground state of Pb^{2+}. The above question can now be rewritten in a different way. Could the APES of the ${}^3T_{1u}$ level be sufficiently changed by the close-by presence of a M^{2+} ion so that the A_X emission is induced and the A_T one is suppressed?

Indeed, the optical properties, i.e., peak position, bands intensity, etc., of these two emissions depend on the kind of impurity and the host lattice, as reported for a number of ns^2 ions in alkali halides. This behavior has been analyzed by Fukuda[2] and Ranfagni *et al.*[3–5,17] within the theoretical framework which includes spin-orbit coupling and linear Jahn-Teller interaction, showing that the shape of the APES can be expressed in terms of two parameters $A=12\xi(1-\beta)/b^2$ and $g=G/\xi$, where ξ and b^2 are, respectively, the spin-orbit and electron-lattice interaction parameters, β is the difference in curvature between the excited and the ground APES's and G the exchange energy. It has been shown[2,17] that small changes in the values of those parameters induce drastic changes in the APES shape.

For NaCl:Pb^{2+},M^{2+} systems, it has been now observed that the electron-phonon coupling constants are affected by dipole aggregation as inferred for the change in the Jahn-Teller splitting of the A absorption (excitation) spectrum. The magnitude of that splitting (Fig. 4) shows a variation of a factor of 1.5 on going from isolated dipoles (A_T emission) to clusters (A_X emission).

Since the splitting is linearly related to the coupling constant c to the T_{2g} vibrational mode this constant should, therefore, change for the same factor of 1.5 on going from dipoles to clusters. Although it may be rather speculative, one can assume that the coupling constant b to the E_g mode experiences a similar change. In fact, simple estimates for b and c by Toyozawa *et al.*[18] based on polarizable point ion charges show that b/c ratios are almost exclusively dependent on the elastic coefficients of the host crystal. Under this assumption, clustering of Pb^{2+} ions should induce changes of a factor of 2–3 in b^2 and consequently in A. According to Fukuda's[2] and Ranfagni *et al.*[17] calculations, a change of a factor of 2–3 in the A parameter can substantially modify the shape of the APES. In particular, such an increase in A (associated to the increase in b^2) is able to change an APES having single shallow minima at T to have rather deep minima at X. Certainly, the presence of the close-by impurity in the aggregates may also alter other parameters, such as β. However, this would not invalidate the above conclusion and moreover, since no direct experimental evidence on such an effect is available, estimative calculations cannot be made.

The previous argument can be reinforced if one considers quadratic terms in the Jahn-Teller coupling Hamiltonian. Ranfagni *et al.*[17] have shown that depending on the value of the quadratic coefficient one can go from a situation where there are T minima with close lying reservoirs to another one with X minima and reservoirs. It is to be expected that the effect of the close by impurity influences the quadratic coupling coefficients at least as strongly as the linear ones.

One additional piece of information suggesting that different APES structures apply to free or clustered Pb^{2+} dipoles arises from the constancy of the A_T and A_X emission intensities in the 10–200-K temperature range. This is at variance with cases such as KBr:Ga^+ (Ref. 19) where the two minima are supposed to coexist and complete interconversion between both emissions occurs. Therefore, the data indicate that the T and X minima do not coexist for Pb^{2+} in NaCl.

Finally, one should comment on the levels lying below the T and X minima. It is also well known that the ${}^3A_{1u}$ level of Pb^{2+} ions also has a complex structure with two minima in the APES closely lying below those of the ${}^3T_{1u}$ level. The lifetime data can be analyzed in terms of photon transitions between these two close levels and the ground state as well as the nonradiative transitions between them, in a similar way to that for KBr:Ga^+ (Ref. 19). The observed fast component is attributed to the allowed transition ${}^1A_{1g}\leftarrow{}^3T_{1u}$ and the slow component to the forbidden ${}^1A_{1g}\leftarrow{}^3A_{1u}$.

The experimental temperature dependence found in this work is in accordance with this scheme, and the temperature changes are connected with nonradiative transitions between the ${}^3T_{1u}$ level and the reservoir ${}^3A_{1u}$, whose distance can be obtained from Figs. 7 and 8, values which are 0.05 and 0.02 eV independently of the codopant impurity.

It is noteworthy that for the A_X emission, this energy gap equals the value of the peak shift (Fig. 2) and which appears at the temperature where the lifetime begins to shorten, i.e., when the upper level begins to be operative. In other words, at low temperature, the emitting level is the ${}^3A_{1u}$ and at temperatures above T_Δ the emission occurs from the ${}^3T_{1u}$ level. Unfortunately, a similar behavior has not been observed in the A_T emission possibly because both levels are equally populated.[15]

The main conclusion of this work is that the luminescence behavior of NaCl:Pb can be rationalized in terms of Fukuda's model. Moreover, the discussion here presented conciliates the (well-documented) fact that the dipoles and small aggregates have different and well-defined emissions at 310 nm and near 380 nm, respectively, with the attribution of them to transitions from two different minima in the APES of the ${}^3T_{1u}$ level.

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