PHYSICAL REVIEW B VOLUME 35, NUMBER 6 15 FEBRUARY 1987-II

Optical spectroscopy of Pb^{2+} in doubly doped KCl:Sr(Pb): Detection of Sr precipitates

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(Received 14 July 1986)

The absorption and luminescence of Pb^{2+} in the A band region ($^1A_{1g}\rightarrow{}^3T_{1u}$) have been studied in KCl:Sr(Pb) ($C_{\mathrm{Sr}}=800$ ppm, $C_{\mathrm{Pb}}=5$ ppm) as a function of thermal treatments leading to different aggregation-precipitation stages of strontium impurities. Quenched samples show two well-defined bands peaking at 340 and 413 nm which have been associated with the A_T and A_X emissions within the framework of the Fukuda model. Dynamical structure on the excitation spectra of these bands has been studied by the second-derivative technique showing that both bands present a temperature-sensitive doublet that responds to a dynamical Jahn-Teller effect as reported for Pb^{2+} in other alkali halides. On the other hand it has been shown that Pb^{2+} is a good optical probe to study Sr precipitates, indicating that $SrCl_2$ develops by annealing the samples in the temperature range 100—250 °C. Long-time annealing at room temperature and in the range 250—300 °C produces other Sr precipitates which can be well characterized optically. By taking advantage of these results the optical spectra of Pb^{2+} in $SrCl_2$ precipitates formed inside the KCl matrix have been studied.

I. INTRODUCTION

It is well known that optical properties (absorption and luminescence) of Pb^{2+} ions are very sensitive to a crystalline environment when these ions are incorporated as impurities in alkali halides.[1-7] These ions are Tl^{+}-like, having a ns^2 configuration and showing the three well-known A,B, and C absorption bands in order of increasing energies. The majority of the reported data is related to the A band ($^1A_{1g}\rightarrow{}^3T_{1u}$) because its position is the most accessible to conventional spectrophotometers. Taking advantage of its crystal-environment sensitivity, absorption and luminescence of this ion (in the A-band region) have been used to investigate the nature of different Pb^{2+} precipitates in a number of alkali halide matrices, by following the optical changes as a consequence of the precipitation process.[6,7] Moreover, as it has been shown during the last years, divalent lead can also be used to probe optically the precipitation phenomena of other divalent cation impurities which do not present optical spectra if a small amount of Pb^{2+} (5 ppm) is incorporated as a codopant in a number of NaCl:M(Pb) systems ($M^{2+}=Ca^{2+},Sr^{2+},Cd^{2+}$).[8-11] It has been established that lead ions are incorporated into M^{2+} precipitates formed through suitable thermal treatments; their presence has been detected from the absorption and emission spectra of the doubly doped samples. The results obtained were consistent with those obtained by using direct techniques, such as x-ray diffraction.[12-14] The new technique has the advantage of using a lower impurity concentration, allowing the detection of new phases not previously reported.

On the other hand, recently reported experimental information has been extensively used to interpret the luminescence of Pb^{2+} in NaCl in terms of the so-called Fukuda model.[15] This model takes into account the possibility of two nonequivalent minima in the adiabatic potential energy surface (APES) of the $^3T_{1u}$ excited level induced by the combined effect of spin-orbit coupling and Jahn-Teller interaction. Then, the emission spectrum of Pb^{2+} under excitation in the A band consists of two emissions which are usually leveled A_T and A_X. This model was also recently proposed to be operative for KCl:Pb crystals, although the A_X emission was practically unobserved.[16]

Taking into account the above comments the purpose of this work has been twofold. First we have used the optical properties of divalent lead in the A-band region ($^1A_{1g}\rightarrow{}^3T_{1u}$) to study Sr precipitates in KCl, where the information about the nature and stoichiometry of these precipitates is not conclusive.[17] Our results reveal that $SrCl_2$ particles develop by annealing our samples at high temperatures (100—300 °C) and that other Sr precipitates, whose nature is unknown, are detected. Second, we present new experimental data to interpret the optical bands of Pb^{2+} in KCl:Sr(Pb) crystals in terms of the Fukuda model.

II. EXPERIMENTAL PROCEDURE

Single crystals of KCl doubly doped with Sr^{2+} and Pb^{2+} were grown in our laboratory by the Czochralski method under a controlled atmosphere of dry argon. The concentration of impurities was determined by atomic absorption spectroscopy as being 5 ppm (atomic) of Pb^{2+} and 800 ppm of Sr^{2+}. Thermal quenching treatments were performed by heating the samples at 550 °C for $\frac{1}{2}$ h and then cooling them onto a copper block at room temperature. Annealing treatments were carried out in a standard furnace with a temperature control in the range ±5°.

Absorption spectra were taken in a Cary 17 spectrophotometer and photoluminescence measurements were made with a Jobin-Yvon spectrofluorimeter, model JY3CS. Second derivatives of the excitation spectra were performed on data from samples with optical density less than 0.3 (in order to avoid saturation effects). Temperature control was made with a closed-cycle helium cryostat (11—300 K) and with a specially designed cryostat [liquid-nitrogen-temperature (LNT) measurements]. X-ray measurements were performed in a Philips model PW 1410 x-ray diffractometer (Instituto de Física, Universidad Nacional Autónoma de México), using graphite-monochromatized Cu radiation. Additionally, the (400) reflection of KCl was attenuated with a slit device of 1/30° of angular divergence.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Pb^{2+} as an optical probe to study strontium precipitates in KCl

In order to detect possible precipitated phases in KCl:Sr crystals, we have introduced during the growth process a small quantity (5 ppm) of Pb^{2+} ions. Evolution of the absorption and luminescence spectrum of Pb^{2+} has been studied for KCl:Sr(Pb) samples under different thermal treatments to get information about the Sr^{2+} precipitates formed during these treatments.

1. Samples after quenching

As a starting point to be able to follow the precipitation process, the optical properties of quenched samples were investigated. In this case the impurity should be initially in its most dissolved form.

The absorption spectrum of these samples is very similar to that reported for KCl doped only with Pb^{2+}. It consists of the Pb^{2+} A band, peaking at 270 nm (width 0.10 eV), and it is associated with impurity-vacancy dipoles and very small aggregates (dimers, trimers, etc.) (Refs. 5 and 6). Excitation inside this band produces two emissions at 340 and 413 nm (Fig. 1). These two bands are in agreement with the previous results obtained for KCl:Pb crystals[1–6] and they have been respectively interpreted as the A_T and A_X emissions in Fukuda's double-minima model.[16] However, the intensity relationship between them in our KCl:Sr(Pb) crystals is in contrast with the one obtained in solely-lead-doped crystals (with the same lead concentration) for which the low-energy emission (A_X) can be hardly detected. Then we can interpret the markedly enhanced ratio I_X/I_T as due to the presence, in our quenched samples, of mixed Sr^{2+}-Pb^{2+} clusters, as a result of the high Sr^{2+} concentration which avoids the total dissolution of the impurity. In fact, this kind of M^{2+}-Pb^{2+} mixed centers has been already reported to occur in NACl:M(Pb) quenched samples for a variety of M^{2+} cations (M=Pb,Ba,Ca,Sr) (Refs. 15 and 18) using photoluminescence, and more directly in NaCl:Sr(Eu), where Sr^{2+}-Eu^{2+} clusters were observed by means of electron paramagnetic resonance.[19]

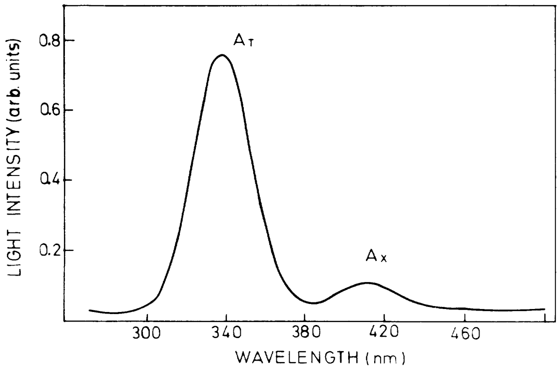

FIG. 1. LNT emission spectrum of a quenched KCl:Sr(Pb) sample under excitation at 270 nm (A band).

In our crystals, the Sr^{2+} ions in mixed centers change in some way the potential barrier separating the A_T and A_X minima of the excited $^3T_{1u}$ level of Pb^{2+}, increasing the A_X emission. In fact, this behavior was seen previously in KCl:Pb crystals, where the coexistence of A_T and A_X emissions was demonstrated for the case of Pb^{2+}-Pb^{2+} clusters.[16]

2. Annealed samples

To induce the formation of Sr^{2+}-precipitated phases the quenched samples were treated at different annealing temperatures, following in each case the behavior of the lead spectra.

(a) Room temperature. While the absorption spectrum of Pb^{2+} only shows a small decreasing and a light broadening during room-temperature (RT) annealing, even after 1500 h of treatment, a new broad emission band peaking at 450 nm is clearly seen to develop. This emission and its corresponding excitation spectrum are displayed in Fig. 2. Inspection of this figure reveals that the excitation band peaks at 280 nm, which is different

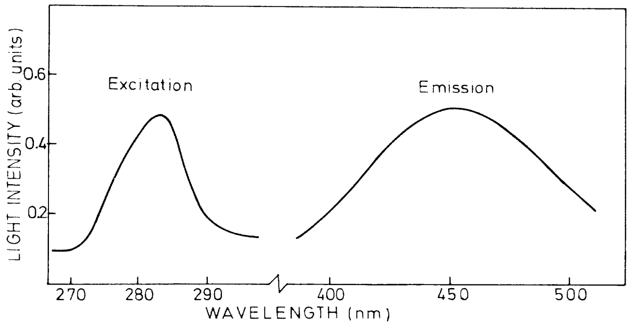

FIG. 2. LNT excitation and emission spectra of a KCl:Sr(Pb) sample annealed 1500 h at room temperature.

from the absorption (excitation) band of quenched samples.

The above-mentioned emission band at 450 nm is not observed in KCl:Pb crystals under the same thermal treatment and similar lead concentration (10 ppm). Thus, this emission should be interpreted as due to Pb^{2+} ions which are incorporated now in Sr^{2+}-precipitated structures. The nature of these precipitates cannot be determined for the time being. This behavior is consistent too with the decrease observed in the *A* band of Pb^{2+} during the annealing.

(b) High temperatures. Annealing treatments at temperatures in the range 100—250°C lead to quite different results from those discussed up to now. Figure 3(a) shows the evolution of the LNT absorption spectra in the *A*-band region for a sample annealed at 250 °C. A decay in the 270-nm band (quenched samples) appears to take place benefiting the formation of a new prominent sharp band peaking at 249 nm (width 0.07 eV). For the longest annealing times, another band at 260 nm begins to appear. We have associated the 249- and 260-nm absorption bands to Pb^{2+} ions incorporated in some Sr precipitates developing within the KCl matrix for this thermal treatment.

In order to obtain additional information about the nature of the precipitates responsible for these absorption bands, the corresponding emission spectra were taken and they are displayed in Fig. 3(b).

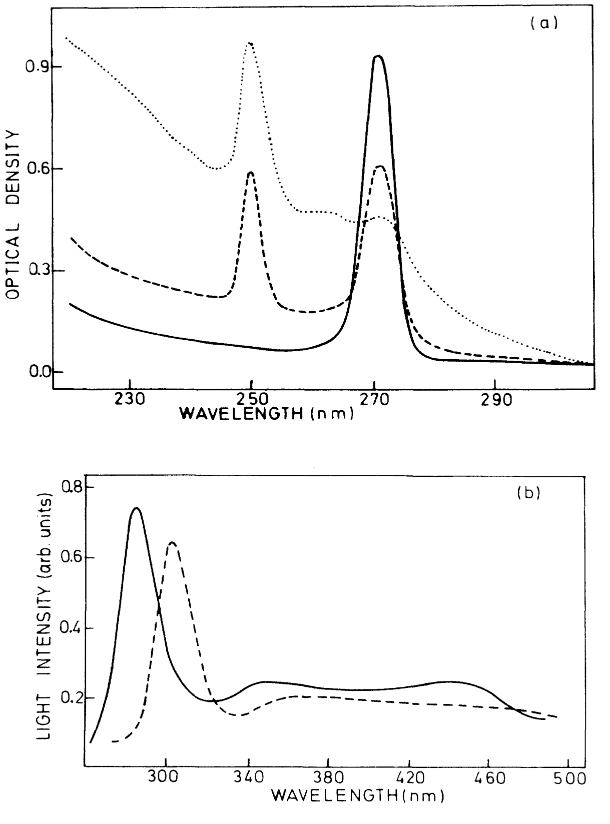

FIG. 3. (a) LNT absorption spectra of a KCl:Sr(Pb) sample for different annealing times at 250 °C. (——,0 h, after quenching), (— — —, 55 h), (· · · , 137h). (b) LNT emission spectra of a sample annealed 570 h at 250 °C under excitation at (——) 249 nm and (— — —) 260 nm.

(i) In connection with the 249-nm band, we may say that its position and full width at half maximum are the same as those observed for Pb^{2+} incorporated in $SrCl_2$ precipitates and previously identified in NaCl:Sr(Pb) crystals.[9,10] Moreover, the corresponding emission spectrum shows a band peaking at 287 nm [see Fig. 3(b)], also quite similar to that associated with strontium chloride particles in NaCl. So, we can conclude that, under suitable thermal annealing treatments, the same kind of $SrCl_2$ precipitates develops in KCl:Sr crystals.

To see more clearly the rate of formation of these $SrCl_2$ particles, the kinetics of the process has been represented in Fig. 4 for two annealing temperatures, 150 and 250 °C. Since the total area of the spectra remains constant during the thermal treatment, we have shown the optical density at 270-nm (free impurity) and 249-nm (precipitates) bands versus annealing time. It can be observed that, in the case of isothermal annealing for 250 °C, the process is quicker than for 150 °C, which shows an initial plateau up to 100 h.

X-ray analysis of our samples was also performed during thermal treatment at 250 °C. Figure 5 shows the diffractograms of samples annealed for 5 and 400 h at this particular temperature [see also Fig. 4(b)]. The (400) (attenuated) reflection peak of KCl is shown together with another peaking at $2\theta = 52.4°$, which corresponds to $d = 1.747$ Å. This interplanary space is coincident with that reported for the (400) reflection of $SrCl_2$ monocrystals.[20] So, the $SrCl_2$ precipitates may be oriented to the (100) direction of the KCl crystal matrix, as observed to occur in NaCl:Sr.[14] The intensity of this reflection grows with annealing time as does the 249-nm band. This fact also indicates that this band is due to Pb^{2+} ions incorporated in $SrCl_2$ precipitates.

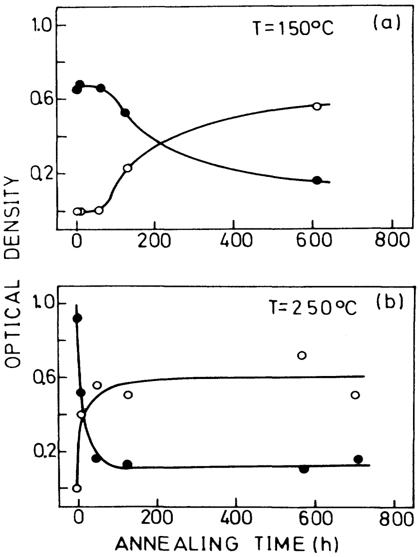

FIG. 4. Evolution of the intensities of the 270- (●) and 249-nm (○) absorption bands versus annealing time for two different temperatures.

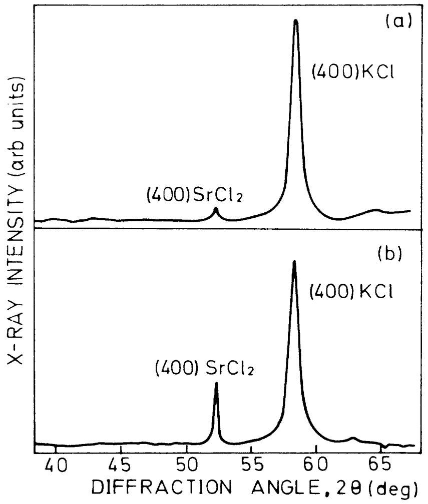

FIG. 5. X-ray diffractograms for a sample annealed at 250 °C for (a) 2.5 h, and (b) 100 h.

(ii) On the other hand, the absorption band at 260 nm has been shown to appear after long annealing times at 250 °C. The corresponding emission spectrum [see Fig. 3(b)] consists of a band peaking at 300 nm. The identification of the Sr phase responsible for this band is not possible with the former method. We propose the use of high levels of Sr concentration to study this phase by means of x-ray diffraction or Raman spectroscopy, in order to determine the structure and stoichiometry of these Sr precipitates.

At this point it would be interesting to compare our results with those previously reported for NaCl:Sr(Pb). We find that the main difference between these two systems is that the precipitation of $SrCl_2$ in NaCl is preceded by the formation of intermediate phases, at variance with the case of KCl where no intermediate states have been detected.

3. *Thermal stability of the Sr precipitates*

After detecting different Sr precipitates in KCl:Sr(Pb) it is possible to study their thermal stability by means of Pb^{2+} absorption bands associated to those precipitates. To carry out this experiment, a preannealed sample (800 h at 250 °C) showing the bands at 249, 260, and 270 nm was used. This sample was heated up to the desired temperature, kept at this temperature for 0.5 h, and then quenched to RT. The corresponding absorption spectrum was examined immediately at LNT. Figure 6 shows the evolution of the 249- and 260-nm absorption bands (measured by the maximum in the optical density) versus temperature. Reference to this figure reveals that $SrCl_2$ precipitates (249-nm band) begin to dissolve at 340 °C, a result very similar to that observed for the same precipitate in NaCl. The Sr precipitate characterized by the 260-nm band is, however, more stable, beginning to dissolve at 400 °C. Figure 6 also includes the evolution of the 270-nm peak due to the dissolved impurity, which, as expected, grows when the other two bands are decreasing. Here we have to say that the thermal stability of the 280-nm band (emission at 450 nm) could not be studied due to masking by the 270-nm band.

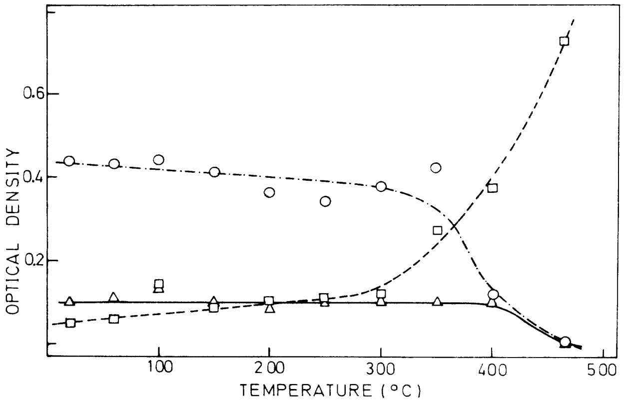

FIG. 6. Thermal annihilation of the the 249-(○) and 260-nm (△) absorption bands and correlated growth of the 270-nm (□) band for a sample annealed 800 h at 250 °C.

B. Dynamical structure of Pb^{2+} bands in KCl:Sr(Pb)

1. *Quenched samples*

We have seen that in our KCl:Sr(Pb) quenched samples, two emission bands (340 and 413 nm) are obtained under excitation at 270 nm. In analogy with KCl:Pb crystals they have been associated with transitions from two minima (A_T and A_X) in the adiabatic potential energy surface of the $^3T_{1u}$ excited level as a consequence of a combined effect of spin-orbit coupling and electron-lattice interaction (Jahn-Teller effect),[16] according to one model initially developed by Fukuda for ns^2-type ions.[21]

The existence of a Jahn-Teller effect for the A band of Pb^{2+} in KCl has been detected by means of the second derivative of the excitation spectrum for the A_T emission band. On the contrary, nothing could be said for the A_X emission due to its weak intensity. However, in our KCl:Sr(Pb) samples the A_X band is much more intense than in the case of solely-lead-doped potassium chloride. This fact allows us to corroborate (by the second-derivative technique) the existence of a dynamical structure in the corresponding excitation spectrum, which is very similar to that observed for the A_T emission in our samples.

Figure 7(a) shows the second derivative of the excitation spectrum for the A_X emission (413 nm) at two different temperatures. A clear splitting can be observed for the higher temperature. Moreover, it has been checked, within experimental dispersion [see Fig. 7(b)], that as expected, the amount of splitting with the square root of the temperature shows a similar behavior to that found for other Pb^{2+}-doped systems,[15,16] which presented a linear dependence typical for a Jahn-Teller effect. In fact, this dependence was clearly observed for the A_T emission in our doubly doped samples as reported for KCl:Pb. Then

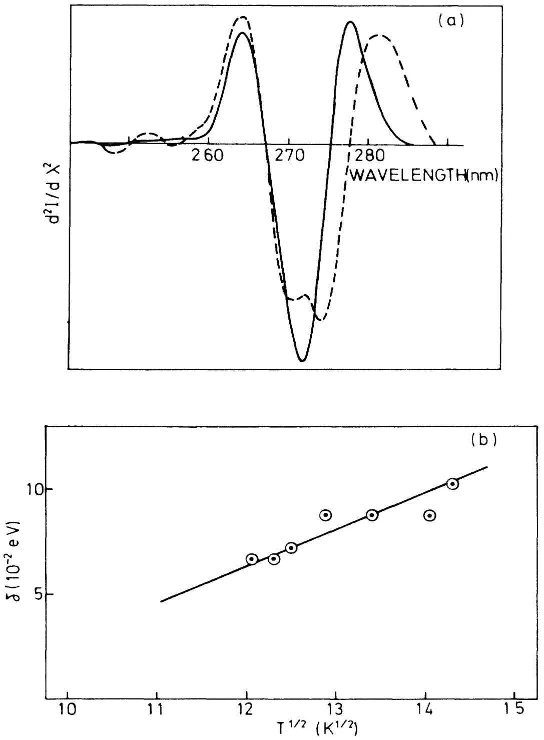

FIG. 7. (a) Second derivative of the excitation spectrum of the A_X emission in a KCl:Sr(Pb) sample after quenching (——, $T=102$ K), (— — —, $T=204$ K). (b) Splitting observed in the excitation spectrum of the A_X emission band as a function of the square root of the temperature for a KCl:Sr(Pb) sample after quenching.

the validity of Fukuda's model is confirmed also in our doubly doped crystals.

On the other hand, the change in the barrier (see Sec. III A 2) between A_T and A_X minima, which is characterized by the increasing intensity of the A_X emission for the KCl:Sr(Pb) crystals, can be now qualitatively explained by taking into account the increasing of the Jahn-Teller splitting ($\delta_{RT}=15\times10^{-2}$ eV) relative to the case of solely-lead-doped samples ($\delta_{RT}=8\times10^{-2}$ eV).[16] This fact could change the Fukuda parameter A as in the case of the NaCl:M(Pb) system,[15] then modifying the height of the barrier.

2. Precipitated samples

Taking advantage of the possibility of introducing Pb^{2+} ions in $SrCl_2$ precipitates we can now study some aspects of its spectroscopy. Unfortunately, to the best of our knowledge, no data on $SrCl_2$:Pb^{2+} system have been reported up to now in the literature, which could be interesting to compare with our results. This fact may be due to the difficulty of growing strontium chloride monocrystals because of their high hygroscopicity.[22]

First of all, it appears reasonable to think that Pb^{2+} ions are located in Sr^{2+} places inside the $SrCl_2$ lattice, as occurs in the case of Eu^{2+} in $SrCl_2$, where it has been proven by means of EPR.[19] In fact, the ionic radii of Eu^{2+} and Pb^{2+} are similar. This is in agreement with the nonexistence of structure in the 249-nm band at low temperatures (11 K), in accordance with the O_h symmetry in which the ${}^3T_{1u}$ excited (Pb^{2+}) level is not split by the effect of the crystal field. But in spite of not having observed structure due to crystal field, we have studied the possible existence of structure in that band due to dynamical effects of the lattice (Jahn-Teller effect) by means of the second-derivative technique on the excitation spectra, as was already observed for Pb^{2+}-doped alkali halides.[15,16,23] This dynamical structure is expected because the ${}^3T_{1u}$ excited level of Pb^{2+} could be coupled with the T_{2g} mode of the $SrCl_2$ lattice as a Jahn-Teller active mode.[24]

In Fig. 8(a) the second derivative of the excitation spectra (emission at 287 nm) for two different temperatures is shown. Reference to this figure reveals a temperature-sensitive doublet structure. The amount of the splitting obeys a function of the form $E=a+bT^{1/2}$ in the range 36—180 K, as can be seen in Fig. 8(b). At about 180 K the emission appears thermally quenched. Moreover, the relative intensity of the two components of the splitting changes with temperature and the reversal of the peak height between these two components occurs at 85 °C. All these facts support the existence of a dynamical Jahn-

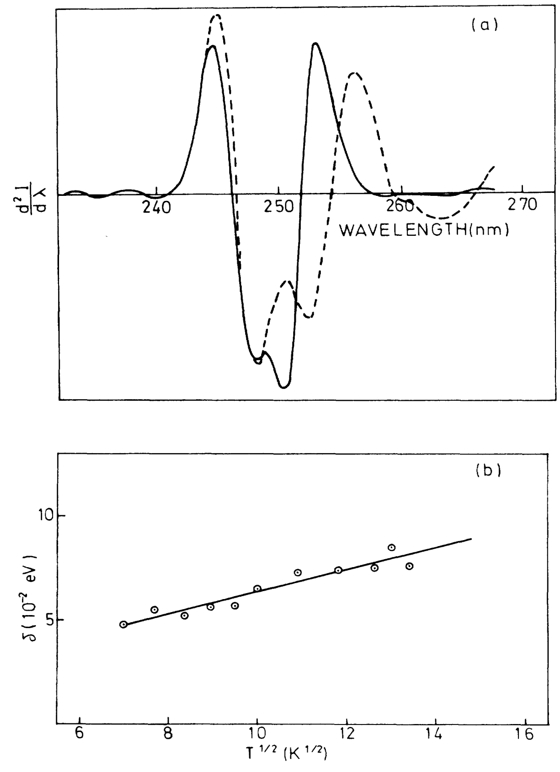

FIG. 8. (a) Second derivative of the excitation spectrum of the 287-nm emission band of a KCl:Sr(Pb) sample annealed 170 h at 250 °C (——, $T=12$ K), (— — —, $T=160$ K). (b) Splitting in the excitation spectrum of the 287-nm emission band as a function of the square root of the temperature for a KCl:Sr(Pb) sample annealed 170 h at 250 °C.

Teller effect for Pb^{2+} incorporated in $SrCl_2$ precipitates.[25,26] Once we demonstrated the Jahn-Teller effect, and in order to explain the optical properties of Pb^{2+} in $SrCl_2$ in terms of the double minima (A_T and A_X) Fukuda model, we examined the emission spectrum for different temperatures in the range 11—300 K. However, no signal of emission other than that at 287 nm was observed. This behavior suggests that no coexistence of the A_T and A_X minima is observed, and only one of these emissions may be operative. In fact, a similar behavior was observed for Pb^{2+}-doped NaCl, where for each configuration only one emission (A_T or A_X) takes place.[15]

IV. CONCLUSIONS

We have demonstrated that the optical properties (absorption and luminescence) of a small quantity of Pb^{2+} ions (5 ppm) can be used to detect Sr precipitates. $SrCl_2$ precipitates develop by annealing the samples at temperatures in the range 100—300 °C. Two other kinds of strontium precipitates, which respectively nucleate at RT and at relatively high temperatures (250 °C) have been detected by this method. The nature of these may be determined by using more direct techniques.

The absorption and luminescence of KCl:Sr(Pb) samples can be rationalized in terms of Fukuda's model and the validity of the model has been definitely confirmed for Pb^{2+} in KCl, because in the doubly doped samples the A_X emission is clearly observed. The optical behavior of $SrCl_2(Pb^{2+})$ crystals has been advanced and a Jahn-Teller effect has been shown to be operative.

ACKNOWLEDGMENTS

The authors are indebted to Dr. Octavio Cano Corona and Mr. A. Clavel for kindly performing x-ray diffraction measurements. We are also very grateful to Professor F. Agulló-López for helpful discussions. This work was partially supported by the Consejo Nacional de Ciencia y Tecnología, CONACYT (México), and the Consejo Superior de Investigaciones Científicas, CSIC (Spain), under Contract No. ICAIESP 800666.

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