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## Aggregation processes in $\text{KCl:Pb}^{2+}$ studied by means of luminescence polarisation analysis

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**Abstract.** An analysis of luminescence polarisation measurements has been performed to study the aggregation processes of  $\text{Pb}^{2+}$  impurities in ionic crystals. The experimental approach was carried out by means of optical measurements (degree of luminescence polarisation, absorption, and excitation and emission spectra) on samples with different impurity concentrations. The analysis of the experimental results was performed following the theoretical calculations performed by Corish *et al* and Bannon *et al*. The theoretical and experimental picture obtained for these crystals explains the first aggregation steps of the ion–vacancy dipoles (in particular, the Suzuki phase formation) and allows us to assign absorption bands to some types of aggregate.

### 1. Introduction

The aggregation processes of divalent impurities in ionic crystals have been studied mainly using the ionic thermocurrent technique (ITC) (Bucci and Fieschi 1964, Bucci *et al* 1966, Radhakrishna and Heridoss 1978), because, at low temperatures, divalent impurity ions associate with cation vacancies to form dipolar complexes (I–V dipoles), and also with electron paramagnetic resonance for paramagnetic impurities such as manganese by Ikeja and Crawford (1973).

Measurements of dielectric loss and thermal depolarisation have shown that the small aggregates result from the association of two or three dipoles called dimers and trimers, respectively (Hor *et al* 1976, Guerrero *et al* 1978). The aggregation of a large number of dipoles yields new aggregates with a higher complexity (Dryden and Harvey 1969, Brown and Jacobs 1973), a metastable Suzuki (1955, 1958, 1961) phase and other precipitated phases. The complexity of the defects depends on the impurity concentration and on the thermal treatments.

The ITC technique is a useful method for following the aggregation process and for evaluating the concentration of small clusters as shown by Koiwa (1974), Unger and Perlman (1975, 1977) and Capelletti (1983) but cannot provide direct information on the structure of the aggregates. A useful experimental approach for obtaining direct information on the structures comes from the analysis with polarised light of the exci-

tation and emission spectra observed for impurities which show absorption and emission bands connected with the aggregates. Such an analysis, which has been carried out for single crystals of NaCl:Pb by Collins and Crawford (1972) and Benci *et al* (1982), supports the attribution of an emission band at 380 nm to an aggregate with trigonal symmetry, probably a trimer of I-V dipoles on the (111) planes.

From the theoretical point of view, there is the interesting and detailed work of Corish *et al* (1980, 1981) and Bannon *et al* (1985) on the calculation of defect energies for the formation and aggregation of I-V dipoles. These workers have proposed an analysis of dipole aggregation starting from the nearest-neighbour (NN) and next-nearest-neighbour (NNN) dipole configurations, selecting the energetically preferred path of aggregation on the ground of the relative stability of the NN and NNN configurations.

Lack of experimental information about the nature of the aggregates has also been noted by Bannon *et al* (1985). The polarisation measurements can provide, in principle, useful information on this problem.

This paper represents an effort to follow and clarify the steps of the aggregation processes starting from the dispersed impurities to metastable Suzuki phase occlusions in KCl:Pb<sup>2+</sup> with a rather low impurity concentration. It must be stressed that the complexity of the absorption and emission bands increases with increasing impurity concentration, owing to the persistence of large aggregates also for well quenched samples. In order to obtain a reliable starting arrangement of dispersed I-V dipoles and to avoid a too fast aggregation process, we chose to work with low impurity concentrations. Previous works by Benci *et al* (1978, 1979), Bertoldi *et al* (1980) and Zaldo *et al* (1982) have indicated the Suzuki phase formation in this system and that isothermal annealing causes modifications of the optical spectra which can be associated with the aggregate formation. The experimental approach was carried out by means of optical measurements (absorption, excitation and emission spectra and luminescence polarisation) of samples with different concentrations aged at a high temperature for different times. The theoretical analysis was performed using the data reported by Corish *et al* (1980, 1981) and Bannon *et al* (1985).

## 2. Experimental details

The experimental measurements of polarised luminescence were performed in a parallel configuration (Benci *et al* 1982). During the measurements the sample were held fixed while the polariser and analyser were rotated.

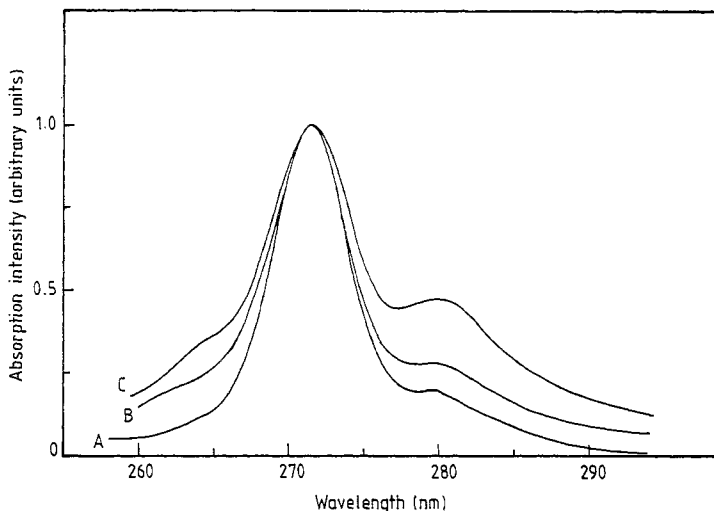
The excitation light was obtained with an Osram XBO 150W/1 lamp, selecting the wavelength by means of a double monochromator. The emitted light was detected with an EMI 9558 QAM photomultiplier and analysed using narrow-band interference filters.

Single crystals of KCl:Pb<sup>2+</sup> containing a lead concentration ranging from 10 to 40 ppm were quenched from 500 °C and annealed at 215 °C for different times.

The optical measurements were made at 80 K.

## 3. Experimental results

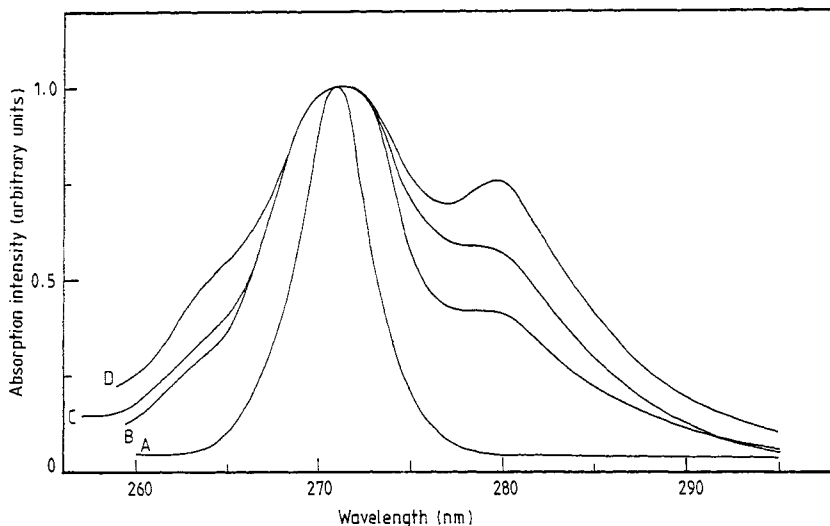
The normalised absorption spectra for the sample with a 16 ppm Pb concentration (figure 1) show new absorption bands at about  $\lambda = 264$  nm and  $\lambda = 280$  nm which



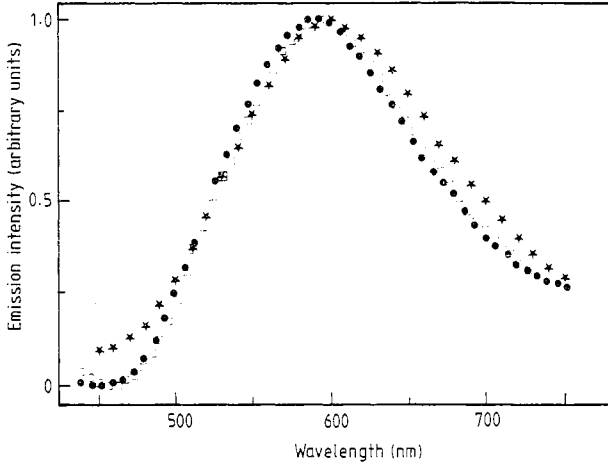
**Figure 1.** Normalised absorption spectra observed at 80 K of a sample with a lead concentration of 16 ppm obtained after 62 h (curve A), 133 h (curve B) and 251 h (curve C) at 215 °C. The absorption coefficients at the normalisation wavelength are  $40 \text{ cm}^{-1}$ ,  $40 \text{ cm}^{-1}$  and  $31 \text{ cm}^{-1}$  for curves A, B and C, respectively.

increase during the isothermal anneal. By increasing the lead concentration, the new bands increase more rapidly with increasing annealing time (figure 2).

The emission spectrum after excitation at  $\lambda = 280 \text{ nm}$  shows a wide asymmetrical band (full width at half-maximum, 0.6 eV) peaked at about 580 nm for all the samples and for different thermal anneals (figure 3). The emission spectrum does not change significantly for excitation at  $\lambda = 264 \text{ nm}$ ,  $\lambda = 275 \text{ nm}$  and  $\lambda = 280 \text{ nm}$  but emphasises



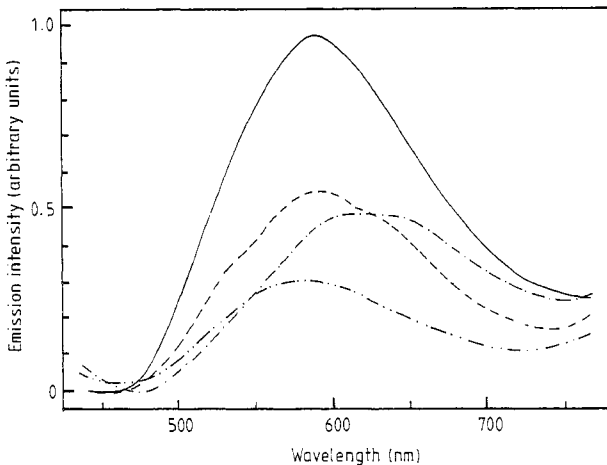
**Figure 2.** Normalised absorption spectra observed at 80 K for a sample with a lead concentration of 40 ppm: curve A, quenched sample; curve B, after 15 h at 215 °C; curve C, after 32 h at 215 °C; curve D after 62 h at 215 °C. The absorption coefficients at the normalisation wavelength are  $100 \text{ cm}^{-1}$ ,  $75 \text{ cm}^{-1}$  and  $75 \text{ cm}^{-1}$  for curves B, C and D, respectively.



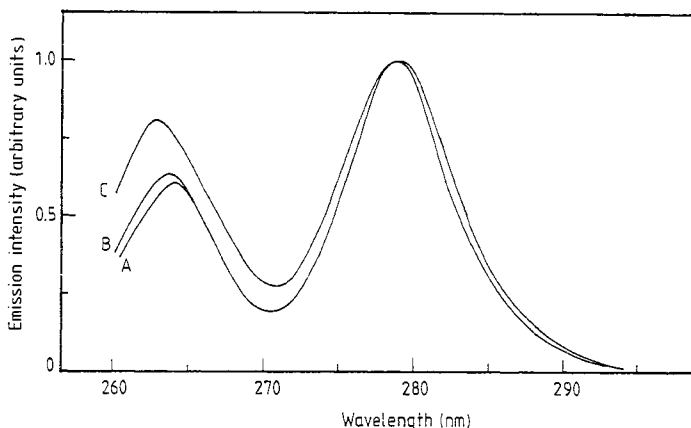
**Figure 3.** Emission spectra at 80 K ( $\lambda_{\text{exc}} = 280$  nm) of a sample with  $[\text{Pb}^{2+}] = 16$  ppm: ★, after 62 h at 215 °C; ●, after 133 h at 215 °C; □, after 251 h at 215 °C.

different contributions while for excitation at  $\lambda = 285$  nm a new band at low energies occurs (figure 4). The same results are obtained for excitation with polarised light. The absorption and emission results agree with those obtained previously for KCl : Pb crystals (Benci *et al* 1979, Bertoldi *et al* 1980) with different impurity concentrations and different annealing times. Bertoldi *et al* (1980) have observed for high (about 70 ppm) lead concentrations and/or for long annealing times an additional emission band at 680 nm, excited at 287 nm.

Figure 5 presents the excitation spectrum of the emission at  $\lambda = 580$  nm for the sample with an impurity concentration of 16 ppm Pb. The same behaviour was observed for samples with different impurity concentrations. The excitation spectra show that this band is not excited at  $\lambda = 272$  nm where the dipoles absorb and that the excitation efficiency increases on increasing the annealing time.

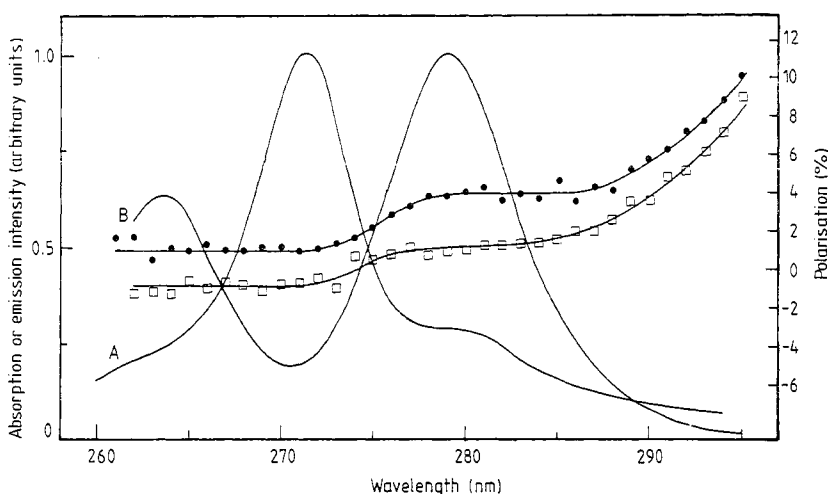


**Figure 4.** Emission spectra at 80 K for a sample with  $[\text{Pb}^{2+}] = 16$  ppm after 251 h at 215 °C: ····,  $\lambda_{\text{exc}} = 264$  nm; —,  $\lambda_{\text{exc}} = 280$  nm; ---,  $\lambda_{\text{exc}} = 275$  nm; - · - ·,  $\lambda_{\text{exc}} = 285$  nm.

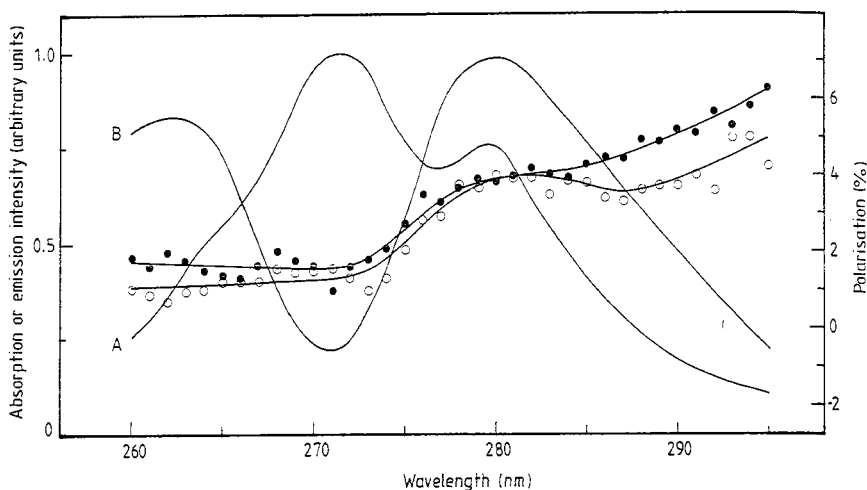


**Figure 5.** Excitation spectrum of the emission at 580 nm at 80 K of a sample with  $[Pb^{2+}] = 16$  ppm after 62 h (curve A), 133 h (curve B) and after 251 h (curve C) at 215 °C.

Polarisation spectra are shown in figure 6. The emission is at  $\lambda = 580$  nm, and the sample (16 ppm  $Pb^{2+}$ ) was annealed at  $T = 215$  °C for 133 h. The same behaviour of the degree of polarisation for  $\alpha = 0^\circ$  and  $\alpha = 45^\circ$  ( $\alpha$  is the azimuthal angle) against the excitation wavelength was measured for all the samples with different lead doping levels and annealed for different times. We can see that the degree of polarisation for excitation at  $\lambda = 280$  nm is higher than for excitation at  $\lambda = 264$  nm and that the degree of polarisation for  $\alpha = 0^\circ$  is lower than that obtained for  $\alpha = 45^\circ$  for the samples with impurity concentrations lower than 40 ppm Pb. For samples with a lead concentration of 40 ppm, the degree of polarisation for  $\alpha = 0^\circ$  is slightly higher than for  $\alpha = 45^\circ$  (figure 7) assuming the same values on increase in the annealing time. Another experimental result which should be noted is that the behaviour of the degree of polarisation depends slightly on



**Figure 6.** Polarisation spectra at  $\alpha = 0^\circ$  ( $\square$ ) and  $\alpha = 45^\circ$  ( $\bullet$ ) for a sample doped with 16 ppm  $Pb^{2+}$  impurities after 133 h at 215 °C. The emission was at  $\lambda = 580$  nm. The absorption spectrum (curve A) and the excitation spectrum (curve B) obtained at 80 K are also shown. Curve B is obtained from the polarisation measurements.



**Figure 7.** Polarisation spectra of 580 nm emission at  $\alpha = 0^\circ$  (●) and  $\alpha = 45^\circ$  (○) for a sample with 40 ppm  $\text{Pb}^{2+}$  impurities after 62 h at 215 °C. The absorption spectrum (curve A) and excitation spectrum (curve B) obtained at 80 K are also shown. Curve B is obtained from the polarisation measurements.

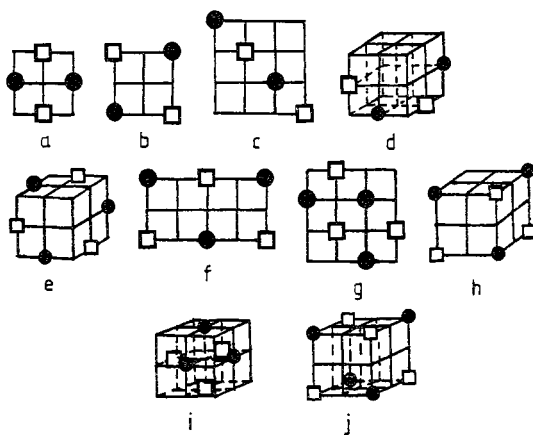
the emission wavelength for excitation at  $\lambda < 285$  nm. For  $\lambda_{\text{exc}} \geq 285$  nm an increased degree of polarisation was measured. This result together with the emission behaviour shown in figure 4 for this excitation and the new absorption bands observed for long annealing times provide evidence of further aggregates. However, also in this case the band overlap is strong and the polarisation is too small to perform an analysis by means of polarisation diagrams.

#### 4. Discussion and conclusions

Let us analyse the aggregation processes (such as the Suzuki phase occlusions) which occur in the formation of large clusters, in order to verify the probable scheme of the aggregation pathway of the dipolar complexes, and also the agreement between our experimental results and the aggregates expected on the basis of the theoretical formation energies computed by Corish *et al* (1981) and by Bannon *et al* (1985). These researchers, starting from the calculation of the binding energy of the I-V dipoles in the NN and NNN configurations, have evaluated the relative stabilities of the two configurations for different impurities also in KCl crystals, disregarding the differences in the association entropy. Using the same approach, they discussed the stability of different types of aggregate and compared the formation energy calculated for the two quoted dipolar configurations. The analysis of the change in the association energies for a particular cluster with respect to different intermediate aggregates can indicate the energetically favoured pathway for the aggregation processes.

From the results of Bannon *et al* (1985) for the divalent impurity ion  $\text{Pb}^{2+}$  in KCl crystals, the relative stabilities of a set of aggregates with different configurations, starting from the I-V dipole defects, can be discussed and compared with the experimental results. The values calculated by Bannon *et al* (1985) indicate that the NN dipoles largely predominate at 25 °C but, if we consider the annealing temperature (215 °C), an

appreciable concentration of NNN dipoles could be expected in our aged samples, and the dimers can also be formed from dipoles with an NNN configuration. The aggregate structures expected in our samples are shown in figure 8. Owing to the rather low impurity concentrations, we can consider that the dimers may form from dipoles, the trimers from dimers by the addition of a dipole, and so on, rather than from isolated constituents (impurities and vacancies). A comparison of the energies of the various aggregates calculated by Bannon *et al* (1985, table 6) with those of the different intermediate defects indicates that the dimeric configuration b in figure 8 (NNN configuration)



**Figure 8.** Aggregate structures expected in  $KCl:Pb^{2+}$  samples: ●, cation impurities; □, vacancies (Corish *et al* (1981).)

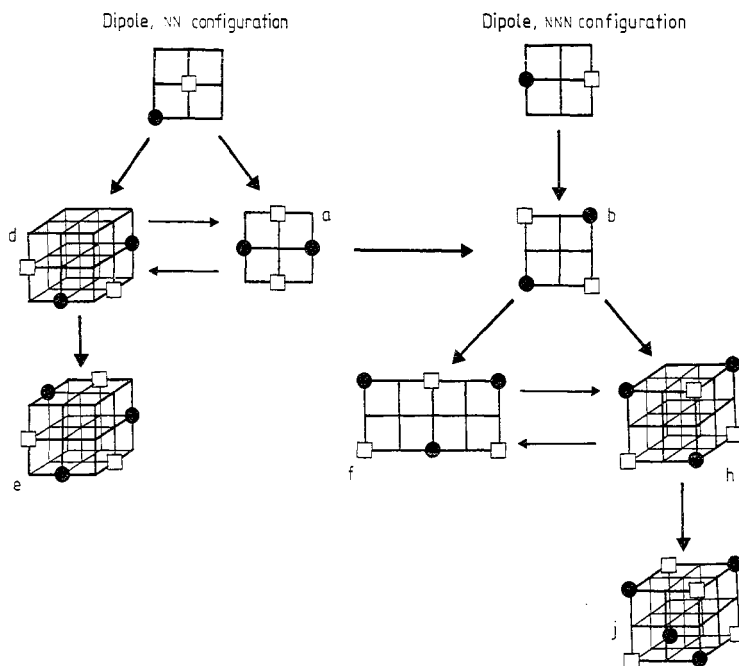
can be considered to be the most stable dimer. The two configurations a and b can be formed with about the same conversion rate, lower than that for NNN dimers. The trimer e (NN configuration) is more stable than trimers f and h. The dimer c and the trimers g and i can almost be neglected. A subsequent step in the aggregation processes leads to the formation of the tetramer j, as a precursor of the Suzuki phase, by the association of the trimers h with one NNN dipole. We believe that the tetramer j can be formed also from the trimer f after its conversion to the trimer h, while for the trimer e with an NN structure the Suzuki phase is not expected to occur.

If one excludes internal conversion between dipoles and aggregates of the two configurations, the concentrations of the aggregates will be mainly determined by the relative concentrations of the dipoles initially present so that, in  $KCl:Pb^{2+}$ , mainly aggregates with an NN configuration should be present. On the contrary, rather fast growth of the Suzuki phase has been well established in  $KCl:Pb^{2+}$  samples annealed at 215 °C also by ITC measurements (Bertoldi *et al* 1980). These experimental results suggest, as emphasised by Bannon *et al*, the possibility of inter-conversion between NN and NNN configurations in the first stage of the aggregation processes (dimer stage), so that the Suzuki aggregates, which are experimentally well established, can be present in a concentration higher than that expected in proportion to the starting concentrations of dipoles of the two configurations. On the basis of the above considerations, we present in figure 9 the probable reactions for the aggregate formation from NN and NNN dipoles in aged samples of  $KCl:Pb^{2+}$ .

Now we can try to associate these aggregates with the new absorption band peaks at



$\lambda = 264$  nm,  $\lambda = 280$  nm and  $\lambda > 280$  nm found experimentally, disregarding the dipoles that do not contribute to the emission at  $\lambda = 580$  nm and taking into account the experimental results on the whole, included the low polarisation values. We observed that these bands increase with increasing annealing time at a high temperature and with increasing impurity concentration. For the two well resolved excitation bands at  $\lambda =$



**Figure 9.** Probable pathway for dipole aggregation in KCl:Pb<sup>2+</sup> samples starting from dipoles in the NN and NNN configurations.

264 nm and  $\lambda = 280$  nm presented in figure 5, we calculated for the full width at half-height a value of 0.13 eV. Such a value provides evidence that these bands could be connected with transitions between electronic levels of aggregate centres broadened by electron-lattice interaction. The band peak at  $\lambda = 264$  nm can be ascribed to a Suzuki phase precipitate as suggested by Benci *et al* (1978) and Bertoldi *et al* (1980). Some other results support this.

- (i) The band peaks at an energy higher than that of dipole band.
- (ii) The band intensity increases more than the band intensity at 280 nm for longer thermal annealing times (figure 5).
- (iii) The degree of polarisation is very low (it can be considered zero) for all the samples examined and for different annealing times (figure 6).

The above arguments agree with a high-symmetry complex such as a cubic centre. In the Suzuki phase the I-V dipoles form occlusions of cubic symmetry (figure 9). The Pb<sup>2+</sup> ion is surrounded by six Cl<sup>-</sup> ions displaced towards the impurity (Bannon *et al* 1985). This displacement can account for the increase in the electronic transition energy with respect to the dipole transition energy.

Because the absorption band peak at  $\lambda = 280 \text{ nm}$  is positioned at an energy lower than that of dipoles, it can be assigned to dimer centres. This assignment is substantiated by the analogy with the case of  $\text{Tl}^+$  in alkali halides analysed by Benci *et al* (1986). In fact, for dimers a and b of  $\text{Pb}^{2+}$ , an electronic energy level scheme very similar to that calculated for thallium dimer centres  $(\text{Tl}^+)_2$  can be expected because the compensating vacancy cannot change the energy level sequence significantly. Following the same picture, we can tentatively attribute the absorptions on the lower-energy side to electronic levels of trimer centres with different configurations (figure 9e, f and h).

Generally, low values of the degree of polarisation can be expected owing to the symmetry of the emitting levels involved in the luminescence processes of these heavy ions in alkali halides (Benci *et al* 1986). In the case of  $\text{KCl}:\text{Pb}^{2+}$  the polarisation results cannot yield exactly the symmetries of the emitting centres. However, the low values for the degree of polarisation agree with the theoretical conclusions. In fact, on the basis of the above arguments, the possible aggregates are a, b, d, e, f, h and j in figure 9. As a whole, their emission is due to a set of transitions with a quasi-cubic symmetry. So, owing to the strong overlap of the absorption and emission bands, the degree of luminescence polarisation will be low and significant values can be reached only for excitation in the tail of the band as results for excitation wavelengths higher than 285 nm (figure 6). However, also for these excitations, the emission is due to several contributions and the degree of polarisation must be explained by means of a combination of centres with different symmetries. The observed behaviours of the polarisation (the degree of polarisation is higher for  $\alpha = 0^\circ$  than for  $\alpha = 45^\circ$ ) for samples with an impurity concentration of about 40 ppm can be explained by different ratios of the intermediate aggregates owing to faster reaction kinetics, as observed for low-doped samples and long-time annealing.

Our effort to obtain direct information on the aggregate structure by means of measurements of the degree of luminescence yields fair results for aged  $\text{KCl}:\text{Pb}^{2+}$  crystals and the agreement between the theoretical and experimental pictures seems very interesting and promising. The theoretical picture of the aggregation steps of I-V dipoles in  $\text{KCl}:\text{Pb}^{2+}$  crystals on the ground of the calculations of Bannon *et al* agrees with the experimental results on the overlap of absorption and emission bands and with the low values of the polarisation; this explains the first aggregation steps of I-V dipoles and the Suzuki phase formation and allows us to attribute absorption bands to some type of aggregate.

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