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Luminescence of Z Centers in KCl:Sr Crystals*

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A search has been made for emissions that are characteristic of the Z_1 and Z_2 centers in additively colored crystals of KCl containing strontium. No emission was found for the Z_1 center. The Z_2 center was found to emit at 1.14 μ at 77°K. A study of the polarization of the emission of the Z_2 center with polarized exciting light leads to the conclusion that this center is of high symmetry.

A study of the transfer of energy between centers that have been formed by irradiating with F light leads to the conclusion that these centers (i.e., F, Z_1, R_1, R_2, M, and a center with absorption at 860 mμ) are formed in the neighborhood of each other.

INTRODUCTION

CERTAIN absorption bands arise from color centers associated with divalent impurities in additively colored crystals of NaCl or KCl doped with strontium, barium, or calcium. These are called Z bands. Pick[1] originally discovered the Z bands and found three of them in KCl and NaCl. The Z_1 and Z_2 bands in KCl were found on the long-wavelength side of the F band at 590 and 635 mμ, respectively, and the Z_3 band was found on the short-wavelength side of the F band at 505 mμ. These bands were resolved from the F band at 77°K. Further work was done on these bands by Heiland and Kelting,[2] Seitz,[3] Camagni and Chiarotti,[4] and Chiarotti, Fumi, and Guilotto.[5] Pick and Seitz proposed different models for the centers responsible for these bands. These are shown in Fig. 1.

It is often possible to determine the symmetry of a luminescing center by exciting it with polarized light and examining the polarization of the emission.[6] Since the proposed models of the Z centers have different symmetry, the present investigation was undertaken to determine if the Z centers luminesce, and if so to study their emission by polarization methods in order to obtain information about the symmetry of the centers.

EXPERIMENTAL PROCEDURE

Sample Preparation

The KCl crystals used in this investigation were grown by the standard Kyropoulos method. Varying concentrations of $SrCl_2$ were added to the KCl melt. Two samples were grown in this manner—one from a melt containing 0.1 molar percent $SrCl_2$ and one from a melt containing 0.01 molar percent $SrCl_2$. Polarographic analysis showed that the more highly doped crystal contained 1.33×10^{-2} molar percent Sr while the other one contained less than 10^{-3} molar percent Sr. Following the initial crystal growth, sections of the crystals were cleaved and additively colored in potassium vapor. The additive coloration was achieved by inserting the crystals in a Pyrex envelope, doubly distilling the potassium, under vacuum, into the envelope containing the crystals, evacuating to about 2×10^{-6} mm Hg, and then sealing the envelope with a helium pressure that was sufficient to prevent the collapse of the Pyrex tube at the additive coloration temperature. The crucible was heated at 600°C for about 24 hours and then slowly cooled to room temperature. The resulting F-center concentration was about 1.3×10^{17} cm^{-3} for both crystals.

Creation of the Z Centers

The Z bands do not normally appear when the crystals are given a rapid quench from the additive-coloration temperature. The Z_1 center can be formed by irradiating an additively colored crystal in the F band at room temperature. The Z_2 center is formed by heating a crystal containing F and Z_1 centers to approximately 110°C. This forms the Z_2 centers, destroys the Z_1 centers, and re-forms a portion of the F centers previously destroyed by the irradiation with F light. This process can then be repeated in order to grow

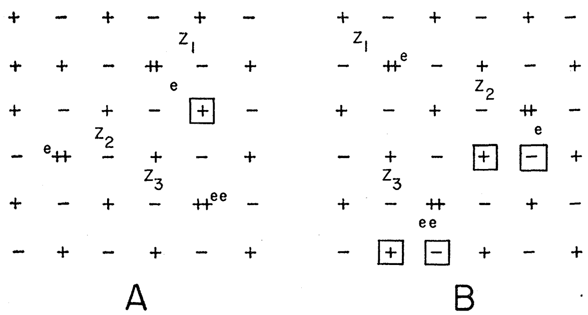

FIG. 1. Models for the Z_1, Z_2, and Z_3 centers. Group A—as proposed by Pick.[1] Group B—as proposed by Seitz.[3] The + and − symbols enclosed by squares represent positive- and negative-ion vacancies, respectively; ++ represents a positive divalent impurity, and e represents a trapped electron.

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[1] H. Pick, Ann. physik **35**, 73 (1939); Z. Physik **114**, 127 (1939).

[2] G. Heiland and H. Kelting, Z. Physik **126**, 689 (1949).

[3] F. Seitz, Phys. Rev. **83**, 134 (1951).

[4] P. Camagni and G. Chiarotti, Nuovo cimento **11**, 1 (1954).

[5] Chiarotti, Fumi, and Guilotto, in *Defects in Crystalline Solids*, edited by N. F. Mott (The Physical Society, London, 1955), p. 317.

[6] J. Lambe and W. D. Compton, Phys. Rev. **106**, 684 (1957).

large Z_2 bands. The Z_3 center can be formed by illuminating an additively colored crystal with F light at -90°C.

As was suggested by Seitz[3] and shown by the Italian group,[5] the Z_2 center can also be formed by slowly cooling the sample from the temperature of additive coloration. The Z_2 centers studied here were formed in this way.

Absorption, Excitation, and Emission Spectra

Absorption measurements were made with a Beckman Model DU spectrophotometer that was modified for measurements at 77°K. The crystal was immersed in liquid nitrogen during this measurement.

Excitation spectra were obtained at 77°K with the crystal immersed in liquid nitrogen.[7] A Bausch and Lomb grating monochromator with a tungsten-lamp source was used for the excitation. The spectral band width of the excitation was 6.6 mμ. A lead sulfide cell in conjunction with suitable filters was used as the detector of the infrared emission.

Emission spectra were taken with a Gaertner quartz monochromator with a lead sulfide detector. The excitations were made with the Bausch and Lomb grating monochromator with either a tungsten or mercury lamp as a source. The spectral band width of the excitation was less than 27 mμ.

Polarization of Luminescence

A schematic representation of the polarization experiments is shown in Fig. 2. The crystal was suspended in liquid nitrogen. The exciting light was either an H-4 mercury lamp or a tungsten lamp filtered to select the particular wavelength required. The first polarizer could be set to excite along either the [100] or [110] direction of the crystal. The emission from the crystal was analyzed by an infrared-transmitting polaroid and detected by a lead sulfide cell. If I_0 is the signal when the direction of polarization of the two polaroids is parallel and I_1 the signal when the direction of polarization of the analyzer is rotated 90° relative to the polarizer, then the degree of polarization of the emission is defined by

$$P=(I_0-I_1)/(I_0+I_1).$$

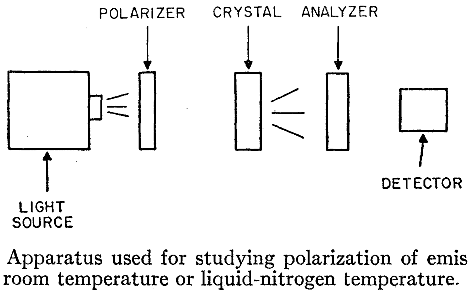

FIG. 2. Apparatus used for studying polarization of emission at room temperature or liquid-nitrogen temperature.

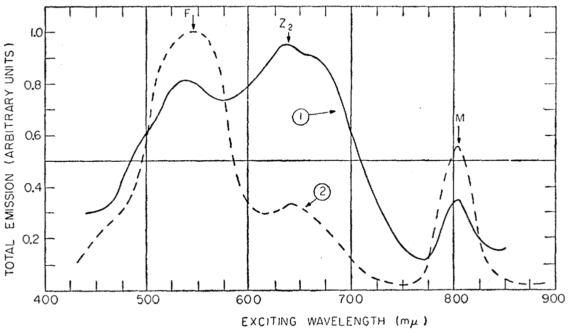

FIG. 3. Total emission at 77°K of an additively colored KCl:Sr crystal as a function of the wavelength of the exciting light. Curve 1—measured immediately after additive coloration. Curve 2—measured after crystal was reheated to 200°C and quenched to room temperature.

DISCUSSION OF RESULTS

Experimental results will only be given for the sample containg the higher concentration of strontium, i.e., 1.33×10^{-2} molar percent. No Z centers were found in the lower-doped crystal that had been slowly quenched. It contained only the same centers found in undoped crystals.[6] Samples of either strontium content contained Z_1 centers after they had been irradiated with F light. The results reported below for the Z_1 centers were qualitatively the same for both samples.

Figure 3 gives the excitation spectrum of two samples that were additively colored as indicated above. Curve 1 gives the results on a crystal immediately after additive coloration. Curve 2 gives the results on a crystal that was reheated to 200°C and then quenched to room temperature. Excitation peaks were found for both crystals at the F (545 mμ), Z_2 (640 mμ), and M (810 mμ) bands. The relative heights of the F and Z_2 bands clearly depend upon the quenching rate.

In addition to the three excitation peaks at the F, Z_2, and M bands, curve 1 shows a peak at about 670 mμ. No evidence of a band at this wavelength was found in absorption measurements taken at 77°K. Since this excitation peak was absent when the crystal was quenched, it is concluded that the center responsible for this excitation has no relationship to the Z_2 center.

Emission spectra were measured for the two crystals of Fig. 3 and were found to be the same. The results are shown in Fig. 4. Curve 1 shows a peak at 1.08 μ with excitation in either the F or M bands. Curve 2 shows a peak at 1.14 μ with excitation in the Z_2 band.

It is known that the M center emits at 1.08 μ and that excitation in the F or M band gives this emission. The excitation of the M center by F-band light is believed to occur by a transfer of energy from the F to the M center.[6]

In the case of the emission at 1.14 μ, it is necessary to determine whether this emission is characteristic of the Z_2 center or results from a transfer of energy from the Z_2 to some other center. Curve 1 of Fig. 3 indicates that some other center may be present that absorbs at

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[7] A technique for making optical measurements on samples immersed in liquid nitrogen is to be published by E. J. West.

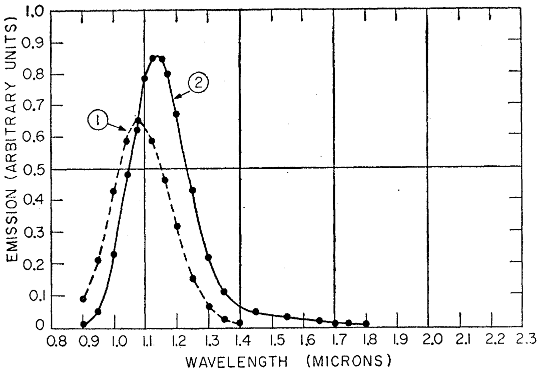

FIG. 4. Emission spectra at 77°K of an additively colored KCl:Sr crystal. Curve 1—excitation in the F (545 mμ) or M (810 mμ) bands. Curve 2—excitation in the Z_2 (640 mμ) band. This was the same crystal as was used for curve 1 of Fig. 3. The ordinate, the number of quanta emitted per unit wavelength, was not corrected for changes in dispersion of the quartz prism monochromator.

670 mμ. However, it has been shown above that the excitation peak at 670 mμ has no direct relationship to the Z_2 band. Further, the same emission (as indicated by peak position and half width) was found with excitation in the Z_2 band whether the excitation peak appeared at 670 mμ or not. Thus, it is concluded that the Z_2 center was not transferring to the center that is excited with 670-mμ light. Since the R_1, R_2, or M centers do not emit at 1.14 μ, the Z_2 cannot transfer to these. We may conclude from this that the 1.14-μ emission is characteristic of the Z_2 center.

Since the 1.14-μ emission is characteristic of the Z_2 center, a measurement of its degrees of polarization with polarized excitation could give information about the symmetry of the center. Z_2 light, whose direction of polarization was along the [100] or [110] direction of the crystal, was used as excitation. In both cases the degree of polarization of the emission was found to be zero, i.e., the emission was unpolarized. This indicated that the center was of high symmetry and implied that of the two models that have been proposed (Fig. 1), the model by Pick is in better agreement with the experimental observations.

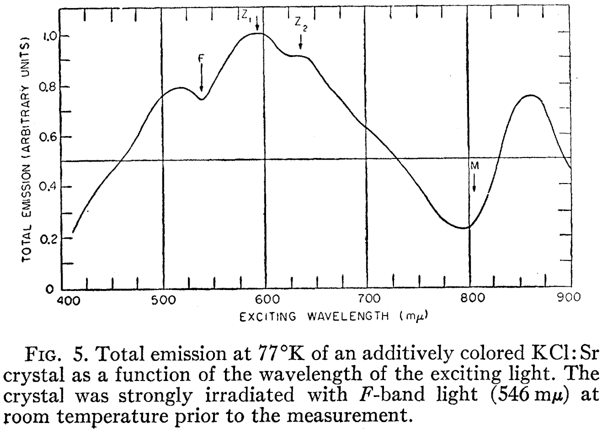

FIG. 5. Total emission at 77°K of an additively colored KCl:Sr crystal as a function of the wavelength of the exciting light. The crystal was strongly irradiated with F-band light (546 mμ) at room temperature prior to the measurement.

Z_1 centers were formed by strongly irradiating with F light a crystal that had been slowly cooled from the additive-coloration temperature. The excitation spectrum of such a crystal is shown in Fig. 5. It is seen that excitation peaks occur in the Z_1 (590 mμ) and Z_2 (640 mμ) bands and at 515 and 860 mμ, but that peaks do not occur at the F (545 mμ) or M (810 mμ) bands. The disappearance of the excitation peak at the M band and the appearance of the peak at 860 mμ did not occur in pure KCl crystals. Thus, it is presumed that the strontium impurity is responsible for this new excitation band. The nature of the center responsible for this is not known.[8] An excitation peak at 515 mμ was found in pure KCl that had been strongly irradiated with F light. Thus, it is presumed that this is not a property characteristic of the strontium-doped samples. However, the nature of the process responsible for this excitation is not known.

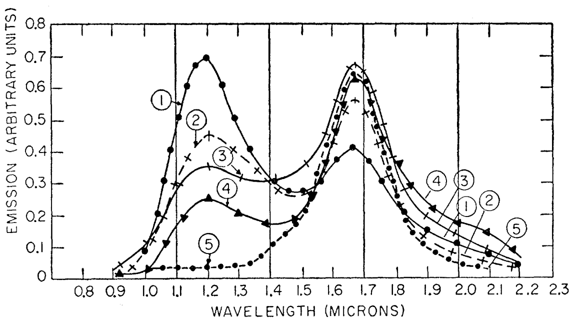

FIG. 6. Emission spectra at 77°K of an additively colored KCl:Sr crystal that had been strongly irradiated with F-band light at room temperature. Curve 1—Z_2-band (640 mμ) excitation. Curve 2—Z_1-band (590 mμ) excitation. Curve 3—F-band (546 mμ) excitation. Curve 4—R_2-band (720 mμ) excitation. Curve 5—860 mμ excitation.

The emission spectra of this crystal are shown in Fig. 6 for excitation in the F, Z_1, Z_2, or R_2 (720 mμ) bands and at 860 mμ. The emissions are similar for all of these excitations. Thus, there does not appear to be an emission characteristic of the Z_1 center and so no information was obtained about the model of this center. Of course, the model of the Z_1 center proposed by Seitz cannot be correct if Pick's model of the Z_2 center is correct.

Some remarks are necessary concerning the two emission peaks shown in Fig. 6. The peak at 1.18 μ is probably a combination of emission from the Z_2 centers (emission at 1.14 μ) and the R centers (emission at 1.23μ). It is likely that R centers are formed during the

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[8] A private communication from G. R. Cole and R. J. Friauf indicates that they have observed an absorption peak at 860 mμ in additively colored crystals of KCl doped with strontium. The band appeared after irradiation with F light at room temperature. They call this the Z_4 band and suggest that the center may be a complex of a positive-ion vacancy and a neighboring strontium that has trapped an electron.

irradiation with F light and that these are excited with F light. Excitation in the Z_2 band overlaps the R-band region, so that with this excitation one might expect to get a combination of the two emission bands. Excitation with 860-mμ light should not excite the R and Z_2 centers since they absorb at higher energies. The peak at 1.68 μ was found with all of these excitations. Since this was the only peak found with 860-mμ excitation, this emission was considered as possibly characteristic of the center that absorbs at 860 mμ.[9] A measurement was made of the polarization of the emission with 860 mμ excitation polarized parallel to [100] and [110]. It was found that

$$P_{[100]}=0.34 \quad \text{and} \quad P_{[110]}=0.39.$$

Although a larger degree of polarization was found for excitation polarized along [110] than [100], it is not possible to represent the center by a simple dipole oriented along [110] for which the degrees of polarization would be

$$P_{[100]}=0.33 \quad \text{and} \quad P_{[110]}=0.66.^{6}$$

The present results give some information about the energy transfer among centers. Lambe and Compton[6] have suggested that energy is transferred between F and M and between F and R centers by dipole-dipole interactions. In order for this to occur with the concentration of centers that was used, it was suggested that the centers were not randomly distributed.

In the unirradiated crystal, excitation in the F or M bands gave emission characteristic of the M center at 1.08 μ while excitation in the Z_2 band gave emission characteristic of the Z_2 center at 1.14 μ. On the basis of the energies of absorption and emission of these centers, it should be possible for an excited F center to transfer energy to a Z_2 center and for an excited Z_2 center to transfer to an M center. Since this is not observed, it is likely that the F and M centers are formed near each other but that the Z_2 center is formed sufficiently far from these other centers that transfer is not possible. Thus, the Z_2 centers appear to be randomly distributed relative to the F and M centers.

Since excitation in the F, Z_1, Z_2, or R_2 bands and at 860 mμ gives emission at 1.68 μ in the irradiated samples, it is likely that this common emission results from a transfer of energy from the excited center to a center whose absorption lies at low energy, perhaps the center responsible for the 860-mμ absorption. Just as F light forms M and R centers near F centers in pure crystals, so Z_1 centers and the centers with absorption at 860 mμ are formed near the F, M, and R centers by F light at room temperature. Thus, it appears that many of the centers that are produced during optical irradiation are formed in a nonrandom distribution.

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[9] The center that absorbs at 860 mμ emits at 1.7 μ at room temperature. The efficiency is about three times as great at 77°K as at room temperature. Excitation in any of the absorption bands gave rise to this emission at room temperature.