NOTIZEN

Absorption Spectra of Pure and Activated β-Zinc Thiocyanate

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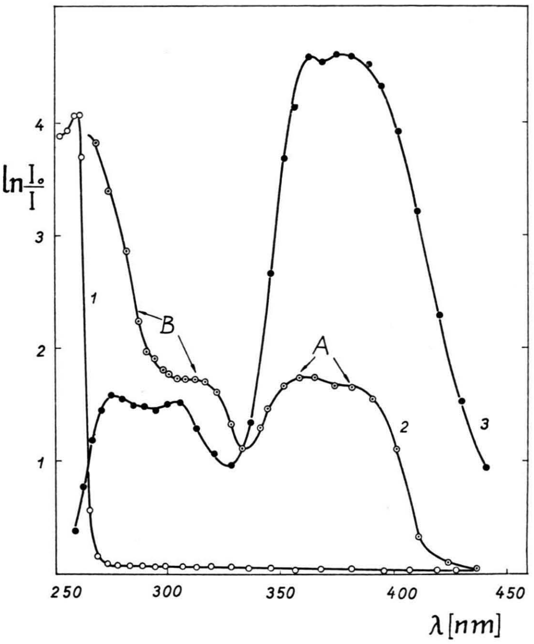
The absorption spectra of the pure and lead activated β-modification of $Zn(SCN)_2$ were investigated. For the width of the forbidden band, 4.7 eV as minimal value is obtained. From the experimental data the conclusion is drawn that strongly localized activator states are responsible for the luminescence. The observed absorption bands can be connected with electron transitions to the $^3P_1$, $^3P_2$ and $^1P_1$ term components of the lead ion.

In previous papers[1, 2] the preparation and the luminescence spectra of lead and tin activated zinc thiocyanate phosphors were described. Later, the existence of two polymorphic modifications, designed as α- and β-zinc thiocyanate, was established, and for the phosphors obtained by their activation considerable differences in the luminescence spectra as well as in the temperature dependence of the emission were found[3]. Our investigations on the α-$Zn(SCN)_2$ phosphors were continued in a work of Dost[4], who studied the luminescence spectra, the activator concentration and impurity ion influence and the temperature quenching of the luminescence intensity. The absorption spectra of α-$Zn(SCN)_2$-Pb were measured in [1] on powders giving rather qualitative data.

In the present paper, some results are reported about the absorption spectra of pure and lead activated β-zinc thiocyanate crystals. Till now we could prepare single crystals of the β-modification only, by slowly cooling from a solution saturated at 90 °C. The lead activated single crystals were grown by adding lead thiocyanate [$3 \cdot 10^{-2}$ mol-% in respect to the $Zn(SCN)_2$] to the solution. The absorption spectra were measured on plates with a thickness of ~ 1 mm, splitted from the single crystals.

Figure 1 shows the single crystal absorption spectra together with the excitation spectrum of a β-$Zn(SCN)_2$-Pb powder sample. On the ordinate axis $\ln(I_0/I)$ is plotted for the absorption spectra, and the emission intensity I in arbitrary units for the excitation spectrum. As it is seen, in the absorption spectrum of Pb^{2+} containing β-$Zn(SCN)_2$ (curve 2) several superposed bands appear, which are absent in the pure crystal spectrum (curve 1). Comparing the absorption spectrum of β-$Zn(SCN)_2$-Pb with its excitation spectrum (curve 3) an exact correspondence is not observed.



By the assumption that the steep rise of curve 1 at ~ 265 nm corresponds to the fundamental absorption edge, one obtains for the width of the forbidden band the value ~ 4.7 eV. In fact, the forbidden band can possibly be wider, if the observed strong absorption at 265 nm is connected with exciton generation.

The absorption spectrum of β-$Zn(SCN)_2$-Pb can be interpreted in a similar way as the spectra of the alkali halide phosphors. Taking into account the analogy between halides and thiocyanates it is reasonable to consider the $Zn(SCN)_2$ crystal lattice as ionic. The existence of activator absorption bands near the fundamental absorption edge shows that the ground activator state is close to the valence band. Then the excited state which is responsible for the green luminescence band ($\lambda_{max} = 485$ nm, $E = 2.66$ eV) should be located at least 2 eV below the bottom of the conduction band. Hence this luminescence should be due to electron transitions between strongly localized states,

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it is an inner-centre luminescence. This is in agreement with the results from dielectric loss measurements showing that Zn(SCN)$_2$-Pb excited with the mercury line 365 nm is not photoconducting.

As known for mercury-like activator ions, a correspondence was established[5] between the electron transition energies in the free ion and in the ion embedded in the crystal: The ion incorporation results in a contraction of the term diagram without disturbing the succession of the terms. In the same way the activator term system in β-Zn(SCN)$_2$-Pb could be affected, regardless of the conjecture[3] that Zn-Pb-SCN-complexes are centres in this phosphor. As far as the β-Zn(SCN)$_2$ lattice seems to have moderate symmetry according to preliminary X-ray diffraction data, there is no reason to suppose that the electron transition $^1S_0 \rightarrow {}^3P_0$ which is allowed by monoclinic symmetry occurs in β-Zn(SCN)$_2$-Pb. In that case, the activator absorption in the longwave UV-region (curve 2, A) could be due to the transitions $^1S_0 \rightarrow {}^3P_1^{(1,2,3)}$ when rhombic lattice symmetry is assumed. The fact that the band groups A and B are separated from each other may be connected with the relatively large distance between the terms $^3P_1$ and $^3P_2$ in comparison with the distance between the components arising by their splitting; this is known for Pb^{2+} in alkali halides[6, 7] and can be expected for Pb^{2+} in β-Zn(SCN)$_2$ also. Thus, in the band group B the longwave elementary bands could be ascribed to transitions to three components of the splitted $^3P_2$ term. The bands superposed in the shortwave part of B can be attributed to the $^1P_1$ term components.

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Mean Amplitudes of Vibration and Coriolis Coupling Constants for Methyl Silyl Acetylene

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Mean amplitudes of vibration, Bastiansen-Morino linear shrinkages and the most important first order Coriolis coupling constants have been calculated for the molecule Methyl Silyl Acetylene. The effect of torsional vibration on the non-bonded mean amplitudes has also been investigated.

Introduction

The complete vibrational frequency assignment for the molecule Methyl Silyl Acetylene was first made by ROBINSON and REEVES[1]. Later DUNCAN[2], in the vibrational study of a series of Silicon compounds performed a normal coordinate analysis for this molecule and reported a set of F matrix elements and coriolis coupling constants. He also pointed out some errors in the vibrational assignment of Robinson and Reeves. As the spectroscopic determination of the mean amplitudes of vibration and the Bastiansen-Morino linear shrinkages[3] could be of great use to future electron diffraction studies, in this paper an attempt has been made to evaluate the above mentioned quantities. Incidentally a qualitative study has also been made to determine the dependence of mean amplitudes of vibration on torsional vibration. The most important first order coriolis coupling constants have also been determined.

Normal Coordinate Analysis

The molecule $H_3SiCCCH_3$ has a staggered C_{3v} symmetry with the normal modes distributed as $7\,A_1 + 1\,A_2 + 8\,E$, the A_2 mode representing the torsional vibration. The A_2 mode is inactive both in Raman and I.R. spectra. The Wilson's symmetry coordinates used in the present work were the same as those given by DEVARAJAN and CYVIN[4] for Acetonitrile-Borontrifluoride. The F matrix elements given by DUNCAN[2] were suitably modified for the newly defined set of symmetry coordinates and properly adjusted so that the eigenvalues of the GF product matrix agreed well with experimentally observed frequencies.

The vibrational frequencies used in these calculations were the ones given by ROBINSON and REEVES[1], with the changes suggested by DUNCAN[2].

Mean Amplitudes of Vibration

The mean amplitudes of vibration and Bastiansen-Morino linear shrinkages were determined by CYVIN's method[3] and the values are given in Table 1. As in a previous publication[4] the torsional symmetry coordinate was also included in the calculation with the hypothetical frequency values 50 cm^{-1} and 150 cm^{-1}. It was found that only gauche H...H non-bonded mean amplitude was dependent on the torsional mode. The linear shrinkages remained unaffected.

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