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VI-9. Analysis of Zero-Phonon-Lines in Absorption and Emission of Copper Impurities in ZnS Crystals

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The origin of a variety of zero-phonon lines in the absorption and emission spectra of ZnS-Cu crystals has been analyzed. Two groups of lines are identified to arise from crystal field splitting of the ${}^2D$ level of Cu^{2+} ions into the ${}^2E$ and ${}^2T_2$ state, which is realized in a hexagonal and a cubic lattice respectively. The observed fine structure can be attributed to an additional lifting of the degeneracy of the ${}^2E$ levels by the action of small field components of lower symmetry. These fields are caused mainly by defined defects due to polytypic effects between the hexagonal and cubic phases. The splitting of the main cubic line is ascribed to a Jahn-Teller effect.

§ 1. Introduction

The incorporation of copper impurities influences the optical and electrical properties of II-VI compounds essentially. The role of copper as a luminescent center in ZnS-type phosphors and as an acceptor level in CdS-type photosemiconductors is subject of a wide range of literature.[1] Detailed experimental and theoretical investigations of the near infrared low temperature absorption spectrum have been carried out with copper doped ZnO crystals.[2] A series of lines has been detected and explained to be due to a splitting of the ${}^2D$ level of Cu^{2+} by crystal field and spin-orbit interaction.

Fine structure of both absorption and emission spectra of ZnS-Cu crystals in the near infrared region has been observed by Broser, Maier and Schulz.[3] In addition to a pronounced phonon structure several zero-phonon lines could be resolved. These spectra are typical of crystals activated with copper by a radioactive method[4] and thus it is likely that— as in the case of ZnO—Cu^{2+} on lattice sites is the responsible center.

The interpretation of these experimental results could not be completed. A small shift of about 20 cm^{-1} between the zero-phonon lines in absorption and emission and the origin of a multiplet structure of these lines was not understood. In addition it proved to be complicated to analyse the phonon structure of the emission spectrum. These difficulties required additional measurements at higher optical resolution using ZnS-Cu crystals with different structures and activated by different methods. Their interpretation according to crystal field theory shows that deviations from the ideal cubic or hexagonal lattice packing must account for the much more complicated structure of the zero-phonon-lines in ZnS as compared with ZnO.

§ 2. Experimental

We mainly used single crystals of ZnS grown in our laboratory.[5] Most of them consisted of a mixture of hexagonal and cubic structures. For a few almost ideal cubic crystals we have to thank Dr. Samelson (General Telephone and Electronics Research Laboratories Inc., Bayside, N. Y.). The incorporation of copper was performed either by neutron induced radioactive activation,[4] using the reaction $Zn^{64} + n \rightarrow Zn^{65*}$ (245d)$\rightarrow Cu^{65}$, or by usual physicochemical methods. Emission and absorption spectra were recorded with the crystals immersed in liquid helium of 4.2 or 1.6°K by means of a Jarrell Ash 1 m spectrometer and by conventional infrared equipment. The emission spectra were excited by visible and near ultraviolet light ($1.5\,\text{eV} \leq h\nu \leq 4.0\,\text{eV}$) producing an indirect excitation of the Cu^{2+} center via the valence band.[6]

The main shape of the complete absorption and emission spectra has already been published.[3] Repeated measurements with several differently structured and differently activated crystals did not show marked deviations in the general view of the spectra. In the overlapping region of absorption and emission however the better resolution gave much more detailed information. In the following we only will discuss the behavior of these narrow zero-phonon lines.

The simplest spectrum is found with the pure cubic crystal (Fig. 1). A single line in absorption is coinciding with the main line in emission at 6927 cm^{-1}, both lines having a half-width of about 2 cm^{-1}. The second line at 6913 cm^{-1}, which appears only in emission depends considerably on the excitation wavelength. Irradiation of the crystal with the entire visible and near ultraviolet region instead of red light only increases the intensity ratio of the 6913 cm^{-1} line to the 6927 cm^{-1} line. A polarization of these "cubic" zero-phonon lines could not be found.

Many more narrow lines are observed if a crystal of the mixed cubic-hexagonal structure is investigated (Fig. 2). Again the main line in absorption and emission appears at 6927 cm^{-1}, but in the nearest neighbourhood at least 6 additional lines are existing. Besides a new group of lines is found with a center of gravity around 6813 cm^{-1}. While the new lines in the neighbourhood of the main cubic one are coinciding exactly in absorption and emission only some of the peaks around 6813 cm^{-1} are observed in both spectra. As the centers of gravity of both

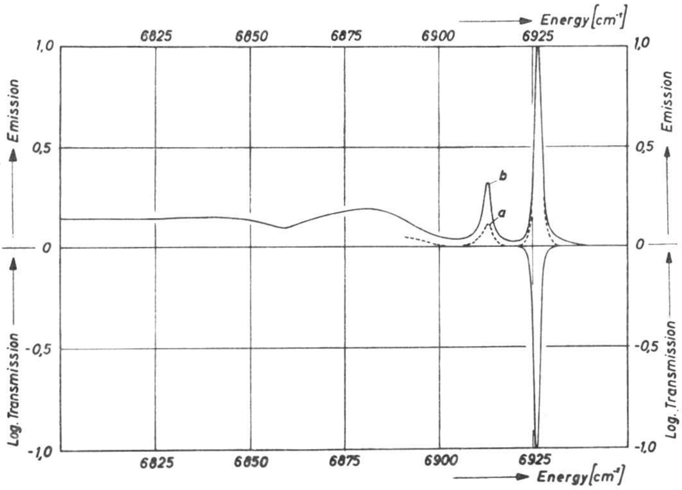

Fig. 1. Emission and transmission spectra of a cubic ZnS-Cu crystal at 4.2°K.
a) excitation $5300\,\text{Å} \leq \lambda \leq 8000\,\text{Å}$
b) excitation $3600\,\text{Å} \leq \lambda \leq 8000\,\text{Å}$

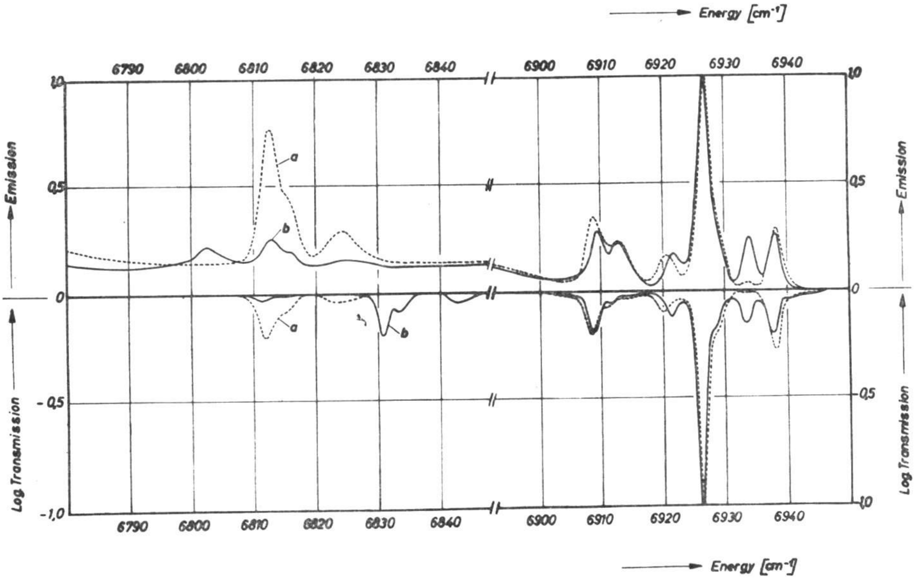

Fig. 2. Fine structure of zero-phonon-lines of a mixed cubic-hexagonal ZnS-Cu crystal at 4.2°K.
a) Polarization $\mathfrak{E} \parallel c$
b) Polarization $\mathfrak{E} \perp c$

line groups are different in absorption and emission, a measurement not resolving the lines must yield the shift of 20 cm^{-1} between corresponding peaks previously recorded.

The polarization properties of the zero-phonon lines can also be drawn from Fig. 2. Again the "cubic" components (6927 and 6913 cm^{-1}) of the short wavelength line group are almost not polarized and the peak at 6913 cm^{-1} is absent in absorption. There is a highly polarized line with $\mathfrak{E}\perp c$ at 6934 cm^{-1} and a second one which either consists of two oppositely polarized lines at 6920.5 and 6921.5 cm^{-1}, or which is peaking at 6921 cm^{-1} with different polarization of the two flanks. The other lines at 6909, 6930 and 6938 cm^{-1} are only weakly polarized but they also have different polarization directions on their flanks. The lines around 6813 cm^{-1} are all strongly polarized, three of them (6813, 6816, 6824 cm^{-1}) with $\mathfrak{E}\parallel c$ and three (6803, 6831, 6843 cm^{-1}) with $\mathfrak{E}\perp c$.

Again the exciting wavelength influences the shape of the spectra. In Fig. 3 the non-polarized emission of another conventionally doped ZnS-Cu crystal is compared with and without short wavelength (≤ 5300 Å) irradiation. By using red light only, all intensities compared with that of the main line at 6927 cm^{-1} have considerably decreased. The non-structured background (≤ 6885 cm^{-1}) due to an interaction of the electronic transition with local modes decreases too, indicating phonons to be mainly coupled to the small side lines. From Fig. 3 the difference in shape of no-phonon and phonon lines can be seen especially clearly. The maximum at 6885 cm^{-1} is considerably broader than the no-phonon lines, there is no longer any reason to assume this line, called E(III) in ref. 3), to be related to a direct electronic transition.

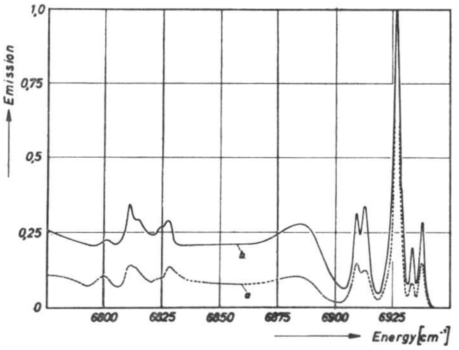

Fig. 3. Emission lines of a mixed cubic-hexagonal ZnS-Cu crystal at 4.2°K.
a) excitation 5300 Å$\leq\lambda\leq$8000 Å
b) excitation 3600 Å$\leq\lambda\leq$8000 Å

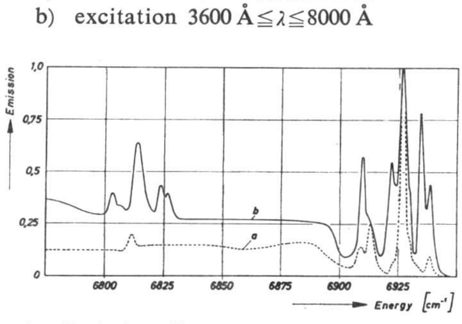

Fig. 4. Emission lines of a mixed cubic-hexagonal ZnS-Cu crystal at 4.2°K.
a) before
b) after annealing for 3 hours at 1150°C

In order to assure that the difference in the spectra for pure cubic and mixed cubic-hexagonal crystals is due to the differences in crystal structure, we annealed cubic crystals at 1150°K for about three hours and cooled them down by successive quenching in water. While a pure cubic crystal showed no effect a remarkable change of the absorption and emission spectra resulted with another not as perfectly cubic and highly doped crystal. The intensity of lines around the main cubic line increased considerably, and in addition the series of peaks around 6813 cm^{-1} turned up.

Further investigations have been done in order to check the dependence of the line structure on temperature. Lowering the temperature to 1.6°K did not show any detectable effect both in emission and in absorption. At temperatures around 60°K the fine structure disappeared and spectra of the form described elsewhere resulted.[6)] In the intermediate range a broadening of all lines occurred but none of the lines disappeared earlier than others. Electric fields of the order of 10^4 V/cm were applied across the crystal. Though a very sensitive recording method was employed no effect could be found. Experiments with high magnetic fields for the observation of Zeeman splittings of the various lines did not yet give clear data.

§ 3. Discussion

As has previously been published the fine structure of the entire emission and absorption spectrum due to the incorporation of Cu^{2+} centers into ZnS can be composed of a few zero-phonon lines and their phonon derivatives. Zero-phonon lines have been assumed to exist in the overlap region of absorption and emission and in the range about 800 cm^{-1} towards lower energies, where only emission lines appear. In accordance with the work of Dietz *et al.*[2] on ZnO-Cu these lines could be attributed to electronic transitions occurring between the levels of the $3d^9$ configuration of Cu^{2+} ions, whose degeneracy is lifted by a cubic tetrahedral field into the ^2E and $^2T_2$ states. (For nomenclature and level scheme see ref. 2)). A further splitting can be understood by a combination of spin-orbit coupling and a trigonal field, thus forming five Kramers doublets. While the two levels split from $G(^2T_2)$ by trigonal fields can only give rise to emission lines, the remaining three levels should originate two electronic transitions $E_{1/2}(^2T_2) \rightleftarrows E_{1/2}(^2E)$ and $E_{1/2}(^2T_2) \rightleftarrows E_{3/2}(^2E)$, which are possible both in absorption and in emission. In this paper we restrict ourselves to the analysis of lines belonging to these transitions. We did not succeed —as a consequence of some broadening not yet understood— in resolving the zero-phonon lines in the long wavelength region of the emission spectra better than before.

a) *Pure cubic crystal*

In a pure cubic crystal only tetrahedral fields should exist and the two Kramers doublets $E_{1/2}$ and $E_{3/2}$ should degenerate to just one. Thus one expects a single line in absorption and emission. In fact from Fig. 1 a very simple structure of the zero-phonon lines can be seen. However, the occurrence of a second line in emission is to be discussed. As a very probable explanation the existence of a Jahn-Teller effect is assumed. Four main arguments for such a case are drawn from experiment:

1) A splitting of the ^2E level by Jahn-Teller effect is possible only in the excited state. Therefore, no absorption line should be observed.[7]
2) The split system must be in the lower excited state. In the upper state no Jahn-Teller effect would be possible. Emission from a Jahn-Teller distorted center thus can occur only if the hole is occupying the lower level. As a consequence only one additional line on the long wavelength side of the main line will result.
3) The dynamical Jahn-Teller-effect is joined to the presence of phonons[8] which are provided by the exciting mechanism. The transfer of Cu^+ centers into Cu^{2+} by the action of blue or ultraviolet light[6] might supply more phonons to increase the intensity of the Jahn-Teller line at 6913 cm^{-1} than the excitation by red light.
4) The possible directions of Jahn-Teller distortion are equivalent. Therefore one cannot except any polarization of the emission line.

b) *Crystal with a cubic-hexagonal polytype structure*

Similar results as for pure cubic ZnS crystals would be expected for pure hexagonal crystals. However, there is almost no experimental possibility to grow such crystals with sufficient amounts of copper. This is due to the fact that hexagonal ZnS can be grown only at temperatures above 1020°C and that it changes to cubic modifications below this transition point. Copper impurities seem to catalyze this transformation considerably.[9] Thus it is likely, that even with high speed cooling of the crystal the region surrounding the copper ions will be transformed into the cubic structure. In fact, most of our crystals are hexagonal polytypes and thus the Cu^{2+} ions will be exposed to lower symmetry components of the crystal field. With mixed cubic-hexagonal crystals two effects should be observed: first, instead of just one "cubic line", another "hexagonal line" should show up. Secondly, these lines should be surrounded by several pairs of lines, representing Cu^{2+} ions in a distorted tetrahedral neighbourhood. Commonly the two lines of each pair should show polarization effects according to group theoretic considerations.

The experimental results seem to correspond to these predictions: In addition to the "cubic" lines at least five more narrow lines in their neighbourhood and a new group of lines shifted towards smaller wavenumbers are observed. For the "cubic group" we assume that the two lines at 6909 and 6938 cm^{-1} as well as the lines at 6921 and 6934 cm^{-1} are pairs of the described type. This is probably correct in view of the following arguments:

1) The intensity ratio of the lines of one pair nearly equals in all crystals.
2) By changing the spectrum either by using a different excitation (Fig. 3) or by annealing the crystal (Fig. 4) the lines belonging to one pair change their intensity by the same factor.
3) One of the two inner lines is strongly polarized $\mathfrak{E} \perp c$ as must be expected in a

center trigonally distorted along the *c*-axis. There are polarization effects also with the two outer lines but their origin is not yet understood.

The situation in the region of the "hexagonal" lines is more complicated. All the lines are polarized and they partly appear only in emission or in absorption. This leads to the conclusion that very few Cu^{2+} ions are situated in hexagonal parts of the lattice with a purely tetrahedral crystal field. Either a small trigonal field component is acting even in the undisturbed hexagonal lattice, as in the case of ZnO (in contradiction to ref. 10)), or the influence of the polytypic structure is so strong, that no undisturbed regions at all exist in our crystals.

In conclusion, there is full coincidence of emission and absorption lines both in energy and polarization. The occurrence of two line groups for the hexagonal and cubic phase could be proved and a fine structure in the neighbourhood of the main lines be explained as a splitting by fields of lower symmetry arising from a polytypic crystal structure. On the other hand the question what special types of deviations are responsible for that effect is still open for discussion. As a consequence of our results it has become clear that the analysis of the near infrared spectra of Cu^{2+} can be used to determine the strength and the symmetries of crystalline fields and from this the crystalline structure of the investigated solid.

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DISCUSSION

Kamimura, H.: Did you determine the spin-orbit coupling constant of the ground state from the observed peak? If you did, could you tell me the value?

Broser, I.: The spin-orbit coupling constant has already been reported in a recently published paper (Phys. Rev. **140** (1965) A2135) to be $\zeta = 593\ \mathrm{cm}^{-1}$ for Cu^{2+} in ZnS. The new measurement showing absorption due to the transition within the $2T_2$-levels, split by spin-orbit interaction, gives rise to a peak at a wavenumber of $810\ \mathrm{cm}^{-1}$, which coincides very well with this value. From this we concluded, that the value of $\zeta = 522\ \mathrm{cm}^{-1}$ for Cu^{2+} in ZnO, given as one of two possible values by Dietz, Kamimura *et al.*, will be the correct one.

Kamimura, H.: Are you saying that the Jahn-Teller effect occurs in the excited ^2E state?

Broser, I.: Yes, indeed, we believe the Jahn-Teller effect occurs only in the excited ^2E state, this explaining the fact that there is only one line present for absorption and two for emission. The reasons for our assignments are given in more detail in the Proceedings.

Ibuki, S.: Do your spectra depend on the sulfur pressure during crystal growth?

Broser, I.: We did not yet investigate the correlation between the growing conditions of the crystals and the shape of the ZnS-Cu^{2+} spectra. During the annealing experiments, the crystals were immersed in a noble gas atmosphere.

Ibuki, S.: Did you check your local structure by the ESR technique?

Broser, I.: Such measurements are being done just now, but the results are not yet available.