sistent with the idea that trace impurities act as electron or hole traps, or recombination centers in the crystal,[11] and that by so doing they shift the steady-state concentration of holes or electrons present during irradiation.

The possibility that lead acts through the electronic system makes the understanding of the radiation chemistry of the Pb impurity crucial. Presumably the lead is initially either a substitutional divalent ion or is covalently bonded to some of the Cl atoms.[13,21] However, since during the first few minutes of irradiation the lead band decreases, it is possible that a different state of lead is involved in the late-stage *F*-center production chemistry at room temperature. There are other pieces of evidence that also suggest that late-stage room-temperature colorability may be influenced by a state modified from that in the grown crystal. We find, for instance, that quenching of a heavily doped sample changes the liquid-nitrogen colorability. Similarly, Schulman[11] found changes in luminescence of NaCl resulting from quenching and room-temperature storage. But in spite of all these effects, no change in room-temperature late-stage colorability or, for that matter, the height of the *A* band was found in our experiments.

ACKNOWLEDGMENTS

We would like to acknowledge the cooperation and care taken by C. A. Pritchard and T. C. Rains of the Analytical Chemistry Division in determining the lead and other impurity contents of many KCl samples. Also, thanks should go to J. R. Russell for his assistance in preparing and growing some of the doped KCl ingots. The continuing interest of J. H. Crawford, Jr., has been very helpful.

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[21] W. J. Fredericks and A. B. Scott, J. Chem. Phys. 28, 249 (1958).

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Nature of the Self-Activated Blue Luminescence Center in Cubic ZnS:Cl Single Crystals

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Over-all optical properties of cubic ZnS:Cl single crystals were studied in order to clarify the nature of the self-activated luminescence center. The characteristic polarizations found both in fluorescence and in thermoluminescence provide the first information about the optical symmetry inherent in the luminescence center in sulfide crystals. From details of the observed azimuthal dependences of the polarization, it is concluded that the luminescence is due to the σ electric-dipole oriented along the tetrahedral bond direction in the cubic lattice of ZnS, and direct evidence is given for the identification of the luminescence center with the *A* center responsible for the electron-spin resonance absorption. There were found two excited states in the polarization spectra, the lower one being located at about 3.42 eV (363 mμ) and the other at about 3.76 eV (330 mμ) above the ground state. According to the observed polarization rules for the optical transitions between these states, the ground state is assigned to an A_1 state, while the emitting state and the second excited state, respectively, are assigned to E and A_1 states belonging to the C_{3v} symmetry center, the luminescence being due to the $E \rightarrow A_1$ transition. Physical pictures of these energy levels are given by simple molecular-orbital treatment on the basis of the model of a Zn^{2+} ion vacancy associated with a substitutional Cl^- ion, as proposed by Prener and Williams, for the luminescence center. The effects of the stacking faults and of possible Jahn-Teller distortion expected in the excited center are also discussed.

I. INTRODUCTION

DURING the past decade, a great deal of effort has been spent in investigating the nature of centers responsible for the various kinds of luminescences in crystals of zinc sulfide and related compounds. In the course of these studies, it has been gradually revealed that some native lattice defects seem to play important roles in the luminescences characteristic of these crystals. Among such luminescences, the origin of the "self-activated" blue luminescence in ZnS has been discussed in a number of papers in the literature. As the atomic models for this center presented up to now one finds an isolated zinc-ion vacancy,[1–5] a zinc-ion vacancy associated with substitutional coactivator ion,[6] or a sulfur-ion vacancy coupled with an oxygen ion.[7] These models, however, were all based either on the results of chemical or heat treatment of the phosphors or on

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[1] R. H. Bube, J. Phys. Chem. 47, 785 (1953).

[2] F. A. Kröger and H. J. Vink, J. Chem. Phys. 22, 250 (1954).

[3] R. Bowers and N. T. Melamed, Phys. Rev. 99, 1781 (1955).

[4] A. Addamiano, J. Chem. Phys. 23, 1541 (1955).

[5] H. Samelson and A. Lempicki, Phys. Rev. 125, 901 (1962).

[6] J. S. Prener and F. E. Williams, J. Chem. Phys. 25, 361 (1956).

[7] N. Riehl and H. Ortmann, J. Gen. Chem. USSR 25, 1057, 1289, 1639 (1955); J. Phys. Radium 17, 620 (1956).

thermodynamical considerations, and could not be more than working hypotheses because of the lack of direct experimental evidence about the atomic structure of the center.

Recently, the first information about the atomic nature of the self-activated luminescence center of ZnS was given by Kasai and Otomo[8] by means of electron-spin-resonance technique under simultaneous irradiation by ultraviolet light. An electron-spin-resonance (ESR) absorption line, which was observed in halogen-doped ZnS, and was designated as "A" signal by these authors, has an axial symmetric g tensor due to a trapped hole. They identified this spin center with the luminescence center and interpreted it in terms of an association model as proposed by Prener and Williams.[6]

However, there seemed to remain some problems in the identification of the spin center with the optical one responsible for the self-activated luminescence. It was thought that it might be related with another defect introduced in the lattice together with the luminescence center. Furthermore, ESR studies can tell only about the energy state in which the unpaired spin resides.

One of the main purposes at the start of the present work was to obtain information about the optical symmetries of energy states involved in the luminescence and also about the nature of electronic transitions between them by means of optical measurements. In the course of the preliminary measurements it was found that a characteristic excitation band exists in the lower energy region of the fundamental absorption edge.[9] This observation had led us to the suggestion that the axial symmetry expected in the luminescence center might be revealed by the measurement of the polarization of luminescence, if one could preferentially excite the luminescence centers having different orientations by means of polarized light excitation in this characteristic excitation band. Some of the preliminary results of such polarization measurements have already been reported in a previous paper.[10]

The present paper deals with further experimental results including polarized thermoluminescence and also polarization spectra. More detailed considerations about the electronic structure of the luminescence center will be presented on the basis of these extended experimental results. In the following, the general characteristics of the self-activated luminescence will be briefly summarized, and then the results of polarization measurements will follow. The last section will be devoted to the detailed discussions about the relation between the observed optical anisotropy and the atomic structure of the luminescence center, and then the physical pictures for the energy states involved in the luminescence center will be inferred on the basis of simple molecular orbital considerations.

II. SPECTRAL CHARACTERISTICS OF THE LUMINESCENCE

1. Emission Spectra

Some of the experimental results and discussions about the characteristics of the self-activated blue luminescence of ZnS:Cl single crystals (kindly supplied by Dr. A. Addamiano, General Electric Company, Cleveland, Ohio) used in the present work have been presented already by the authors' group.[9] These single crystals were grown from the melt, and have cubic zincblende structure with a considerable amount of stacking faults. The summary of the results in the luminescence characteristics will be presented here.

Energy distributions of the luminescence spectra are almost Gaussian in shape. When temperature is decreased, the peak energy of the spectra shifts to lower energies with simultaneous decrease in the half-width as shown in Table I. Such a shift, which is opposite to that of the fundamental absorption edge of the host lattice, is one of the characteristics of the self-activated blue luminescence as pointed out first by Schrader and Larach.[11] The temperature dependence of the half-width obeys the formula which is familiar to both the emission and absorption spectra attributed to well localized center, i.e.,

$$W(T)=W_0[\coth(h\nu/2kT)]^{1/2}. \qquad (1)$$

Although a constant term had to be added, this formula fitted well with the observed data, yielding the value of 2.9×10^{12} sec^{-1} for the frequency ν, which corresponds to that of the local vibrational mode associated with the excited state of the center.

These characteristics all suggest that the optical transitions involved in the luminescence take place within a local center. Following the arguments based on the configurational coordinate model, the peak shift as well as the half-width change with temperature can be explained in terms of the thermal vibration energy associated with the center.[9,12]

Recent measurement of the pressure effect on the

TABLE I. Peak energies and half-widths of the self-activated blue luminescence of ZnS:Cl at various temperatures.

Temp. (°K)	Peak energy (eV)	Half-width (eV)
4	2.60_0	0.28_8
77	2.61_0	0.29_5
192	2.63_2	0.39_6
300	2.64_6	0.45_0

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[8] P. H. Kasai and Y. Otomo, Phys. Rev. Letters **7**, 17 (1961); J. Chem. Phys. **37**, 1263 (1962).

[9] S. Shionoya, T. Koda, K. Era, and H. Fujiwara, J. Phys. Soc. Japan **18**, Suppl. II, 299 (1963).

[10] T. Koda and S. Shionoya, Phys. Rev. Letters **11**, 77 (1963).

[11] R. E. Schrader and S. Larach, Phys. Rev. **103**, 1899 (1956).

[12] S. Shionoya, T. Koda, K. Era, and H. Fujiwara, J. Phys. Soc. Japan **19**, 1757 (1964).

self-activated luminescence[13] could provide another support for the model. When hydrostatic pressure is applied to ZnS:Cl phosphor powder at room temperature, the emission peak shifts from 470 mμ at 0 kbar to 425 mμ at about 38 kbar. The emission peak shift caused by isothermal compression and also that caused by isobar thermal contraction are plotted in Fig. 1 against the change of lattice constant as a parameter in common, which was calculated using available thermal expansion coefficient[14] and compressibility[15] of ZnS. As seen, the directions of the peak shift are opposite in the two cases. This fact seems to indicate that the main cause of the characteristic temperature shift of the emission peak energy is not the thermal expansion of interionic spacings within the center but is the excitation of thermal vibrations in the center as assumed above. Further substantiation of the configuration coordinate model for the self-activated blue luminescence center, together with the details of the pressure effect, will be given in another article.

2. Excitation Spectra

As reported previously,[9] the excitation spectrum of the self-activated blue luminescence is composed of two excitation bands (see Fig. 8). One of them with a sharp maximum at shorter wavelength is evidently correlated with fundamental absorption edge of the host lattice, while the other one, which is characteristic of the self-activated phosphors, is located at the longer wavelength side of the former and is clearly separated from it. This latter band will be designated the "characteristic" excitation band throughout this report, the physical justification of which will be given later.

Relative luminescence efficiencies at these two excitation bands show remarkable change at about 220°K and the characteristic band almost disappears near room temperature as seen in Fig. 8. In order to investigate this effect, the luminescence intensities were measured with varying temperatures under both excitations, i.e., under 315-mμ or 365-mμ mercury light as the host or characteristic excitation, respectively. The results are shown in Fig. 2 in the semilogarithmic plot against the reciprocal of temperature. The abrupt disappearance of the characteristic band clearly corresponds to the remarkable decrease in the luminescence yield by the characteristic excitation at around 220°K as seen in the figure. From the slope of the straight line representing this fast decrease in luminescence intensity, one obtains the value of about 0.64_3 eV as the activation energy for the thermal quenching process. Also, dc photoconductivity measured in the same crystal under the 390-mμ light irradiation shows parallel decrease with the luminescence by the characteristic excitation when temperature is raised.

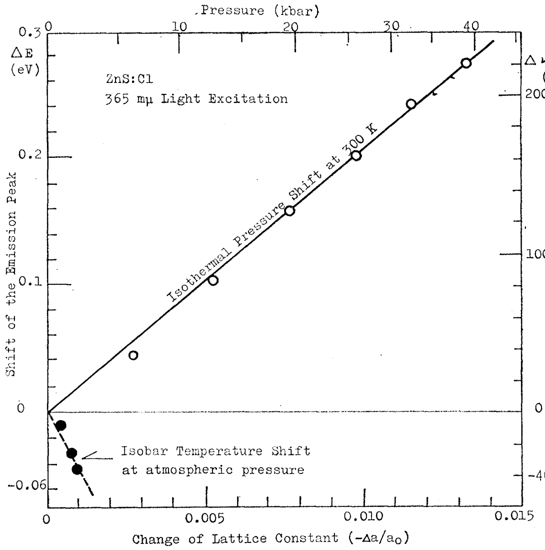

FIG. 1. Shifts of the peak energy of the self-activated blue luminescence of cubic ZnS:Cl crystal. Open circles represent observed shifts caused by the application of hydrostatic pressure at room temperature and filled circles represent the shifts caused by temperature change at atmospheric pressure. Peak shifts relative to the peak energy at 300°K, 1 atm are plotted against the change of lattice constant caused by the compression or by the thermal contraction of the lattice.

3. Other Characteristics

All of the samples used in this experiment showed an intense thermoluminescence at around 110°K. By visual observation, the thermoluminescence was easily identified with the same self-activated blue emission occurring in fluorescence. It was also accompanied by the appearance of a remarkable thermal glow current with a maximum at a temperature somewhat higher than that of the thermoluminescence.

In common with other luminescences in sulfide phosphors, the superposition of infrared light on ultraviolet light at low temperatures causes marked quenching of the luminescence. The quenching spectra by infrared light are shown in Fig. 3. The spectrum at liquid-nitrogen temperature has two quenching maxima, an intense one at about 0.88 μ and a subsidiary one at around 1.42 μ. They are not so prominent near room temperature.

The results of electron-spin-resonance measurements performed using the same crystals as used here have been already reported.[9] Summarizing them, two absorption signals, the same as those designated as *A* and *B* signals by Kasai and Otomo,[8] were found in all samples. Some complicated properties of the *A* signal had been explained in terms of either unequal populations of *A* centers or slight irregularity in lattice arrangement. Because of the importance of these

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[13] T. Koda, S. Shionoya, M. Ichikawa, and S. Minomura, presented to the 1964 spring meeting of the Physical Society of Japan (unpublished).

[14] H. Adenstedt, Ann. Physik **26**, 69 (1936).

[15] P. W. Bridgeman, Proc. Am. Acad. Arts Sci. **76**, 55 (1948).

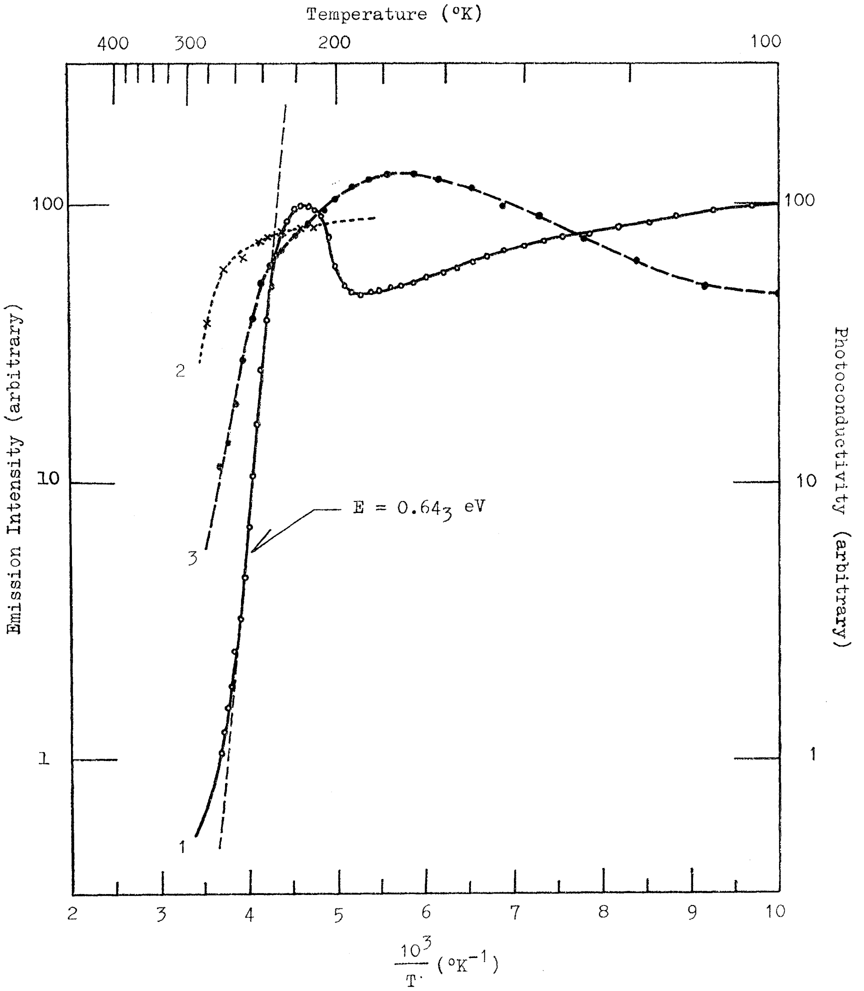

FIG. 2. Thermal quenching of the luminescence and photoconductivity of ZnS:Cl crystal. Curves 1 and 2 represent the emission intensities for the characteristic (365-mμ) and the host (315-mμ) light excitations, respectively. Curve 3 shows dc photoconductivity by 390-mμ light irradiation.

possibilities in polarization measurements, as will be described later, attempts were made to differentiate each component of the *A* lines in ESR absorption spectrum by means of polarized ultraviolet light irradiation. Although some changes were observed in relative intensities of the *A* lines by irradiation with polarized ultraviolet light,[16] the results were not reliable enough to permit one to make a quantitative estimation of the population of spins oriented along each of equivalent directions in the lattice.

Recently, measurements of the decay characteristics of the self-activated blue luminescence were also performed by the authors' group for the same sample by means of pulse-light excitation with a very short duration.[17] The results showed that the decay obeys an exponential law with two components, the time constants being about 0.4 μsec almost independent of temperature for the fast component, and about 4 and 2 μsec for the slow component at 77°K and room temperature, respectively.

4. Discussion

As mentioned before, all characteristics observed seem to suggest that the center responsible for the self-activated blue luminescence is of a well-localized nature. Hence, one may tentatively consider that the characteristic band observed in the excitation spectrum corresponds to the transition by which an electron in the ground state of the center is raised to one of the higher excited states, and that the luminescence is emitted when it returns to the ground state, presumably being the reverse process of the characteristic excitation. The direct experimental evidence that this is indeed the case will be found in the results of polarization measurements as presented later.

The absorption spectra of the same crystals were measured in order to investigate the additional absorp-

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[16] This effect was also pointed out by H. Kusumoto and Y. Otomo, Hitachi Central Research Laboratory, Tokyo, Japan, at the 1963 fall meeting of the Physical Society of Japan (unpublished).

[17] S. Shionoya, K. Era, and H. Katayama, presented to the luminescence symposium, the Electrochemical Society, May, 1964 (unpublished).

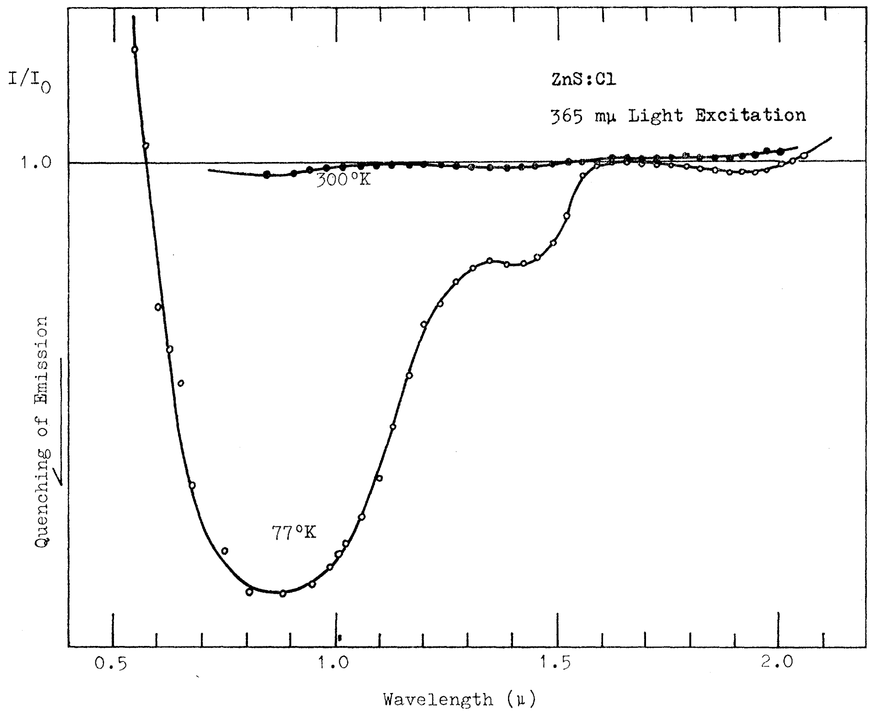

FIG. 3. Infrared quenching spectra for the self-activated blue luminescence of ZnS:Cl at 300 and 77°K, infrared light being superposed on ultraviolet (365-mμ) light excitation.

tion band corresponding to the direct absorption by the luminescence center. A broad absorption band was found at low temperatures at around 3.5 eV (355 mμ) with the absorption coefficient of about 10 cm^{-1}. The quantitative analysis of this band was, however, impossible, due to an appreciable overlapping of the fundamental absorption tail. Probably distorted regions near the stacking faults will have a considerable contribution to the fundamental absorption tail.

The marked thermal quenching of the luminescence observed by the characteristic excitation as mentioned in Sec. II. 2 can be understood as follows: An electron excited by the characteristic excitation light may be freed from the luminescence center with the help of thermal agitation or by the process of autoionization, as will be discussed later. The electron, after migrating in the lattice, will be eventually retrapped by one of the ionized centers where a hole is localized, giving rise to luminescence. Thus, the recombination is entirely due to the radiative transition at low temperatures. As the temperature is raised, however, the hole in the ionized center will have an increasing probability of finding itself in the valence band of the host lattice, thus producing a pair of free electron and hole. Then, because of the large cross section of nonradiative recombination centers of unknown origin, the probability of recapture at the luminescence centers will be markedly decreased resulting in thermal quenching of the luminescence. Since, in the case of host excitation, on the other hand, the electron and hole produced are both free, the nonradiative recombination can take place even at low temperatures in competition with the radiative transition, and one may expect that the thermal quenching in this case will appear at higher temperatures than those in the case of characteristic excitation. This is verified by the observed results shown in Fig. 2, and explains the apparent disappearance of the characteristic excitation band observed at elevated temperatures as seen in Fig. 8. Since the lifetime of free electrons in the conduction band will be decreased when the nonradiative transitions take place, and since photocurrent is carried almost entirely by free electrons in these crystals, the parallel decrease of photocurrent with luminescence intensity as shown in Fig. 2 is consistent with this interpretation.

As a summary of the arguments mentioned here, a model of the energy level scheme is presented in Fig. 4 for the photoelectronic processes in a ZnS:Cl crystal. In this model, it is assumed that the value of 0.64_3 eV obtained before as the activation energy of thermal quenching of the emission corresponds to the thermal depth of the hole in the luminescence center while the peak energy, 1.41 eV, of the infrared quenching band observed at 0.88 μ corresponds to the optical depth of the hole from the top of the valence band. Further details of levels shown in the figure will be discussed in a later section. Since our interest in the present work is concerned mainly with the nature of the self-activated luminescence center, the origin of the electron traps responsible for the thermoluminescence and for the ESR absorption lines is not dealt with here. They might be sulfur vacancies as suggested by Kasai and Otomo,[8] or they might be isolated chlorine ions at substitutional sites.

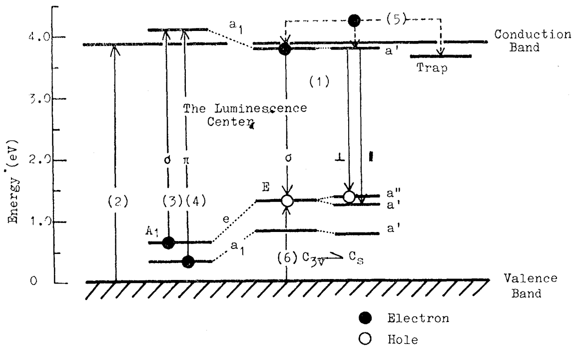

FIG. 4. A model of the energy level scheme for the photoelectronic processes in ZnS:Cl crystal at 77°K. Arrows drawn by solid or broken lines represent optical or thermal transitions of electron, respectively. The luminescence transitions (1) are caused by the host excitation (2) or by the characteristic excitation, (3) or (4). Process (5) represents trapping and thermal ionization of electrons in the trap levels, which is responsible for the thermoluminescence and glow currents. Infrared quenching process is assumed to be the hole transitions (6) from the ionized center into the valence band. Regarding the symmetry notations given in the figure, refer to Sec. IV in the text.

According to the results of the optical Faraday rotation measurements very recently performed by the authors' group,[18] the absorption edge of cubic ZnS is considered to correspond to the direct allowed interband transition at $\mathbf{k}=0$, the energy gaps being about 3.87_1 and 3.75_2 eV at 107 and 286°K, respectively. If one uses these values in the energy-level scheme of the luminescence center, one is led to the conclusion that the location of the excited level which is reached immediately after the excitation has to lie a little above the bottom of the conduction band as shown in Fig. 4. After the relaxation of the lattice surrounding the excited center, the energy of the excited level will be lowered below the bottom of the conduction band and from it the luminescence transition takes place to the ground state. Hence, there might be a probability of the occurrence of autoionization before the excited electron is settled at the energy minimum.

III. POLARIZATION OF THE LUMINESCENCE

1. Introductory Remarks

Since the first observation of the polarized edge emission of CdS by Dutton[19] a number of reports have appeared in the literature concerning the polarized luminescences in ZnS type crystals.[20] However, almost all of the luminescences observed in these reports were polarized perpendicularly to the *c* axis of wurtzite lattice independently of whether the excitation light was polarized or unpolarized, and, therefore, could be correlated with the symmetry of the host crystal as discussed by Birman.[21] Although some luminescences polarized parallel to the *c* axis were reported,[20,22,23] they were either ascribed to the uncertain surface effect[21] or remained unexplained. Thus, up to the present, polarization of luminescence which is ascribed to the optical symmetry of the luminescence center of its own has not been found in ZnS and related crystals.

It was expected at the start of the polarization measurement of the self-activated luminescence that the characteristic excitation band would correspond to the transition which takes place within the luminescence center, and that the preferential excitation of dipoles involved in the luminescence center, which is essential in making polarization measurements as were made in alkali halides[24] and diamond,[25] would be possible by using light in this excitation band.

2. Experimental Procedures of Polarization Measurements

a. Samples. The nature of the cubic ZnS:Cl single crystals used in the polarization measurements has been already described in previous papers[9,10] and also in Sec. II. Because of the high refractive index of ZnS, most of the luminescence light emitted within the crystal may experience multiple reflections and/or refractions before leaving the crystal, by which the original polarization may be changed. After careful examinations, three platelets with dimensions of about 1 mm in thickness and about 6×8 mm in area, which were confirmed to be free from the false polarization effects due to irregularities in shape and structure, were selected from a number of platelets cleaved from the blocks of the melt-grown crystals. These platelets have the $(1\bar{1}0)$ cleavage surface with a $[111]$ axis lying on the plane. This particular axis is perpendicular to the stacking-fault planes and is designated as $[111]_c$ axis, since it is parallel to the polar axis of the faulted region. A sample of cubic shape which has the $(111)_c$ and $(11\bar{2})$ polished planes in addition to the $(1\bar{1}0)$ cleavage surface was also obtained by cutting from the block. Besides these samples, a purely cubic crystal (kindly supplied by Professor S. Narita and S. Sugiyama, Faculty of Engineering, Shizuoka University, Hamamatsu, Japan) which was grown by the method of chemical transport reaction was also used. It has the (100) plane as a natural growing surface.

The sample was fastened to a copper plate by silver paint and was mounted in a metal cryostat. The sur-

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[18] A. Ebina, S. Shionoya, and T. Koda, presented to the 1964 spring meeting of the Phys. Soc. of Japan (unpublished); and T. Koda A. Ebina and S. Shionoya, to be reported at the ICO conference on photographic and spectroscopic optics, Tokyo and Kyoto, on Sept. 1-8, 1964 (unpublished).

[19] D. Dutton, Phys. Chem. Solids **6**, 101 (1958).

[20] For an example, A. Lempicki, J. Electrochem. Soc. **107**, 404 (1960).

[21] J. L. Birman, J. Electrochem. Soc. **107**, 409 (1960).

[22] D. M. Warschauer and D. C. Reynolds, Phys. Rev. Letters 3, 370 (1959).

[23] S. P. Keller and G. D. Pettit, Phys. Rev. **115**, 526 (1959).

[24] For examples, P. P. Feofilov, J. Phys. Radium **17**, 656 (1956); L. Lambe and W. D. Compton, Phys. Rev. **106**, 684 (1957).

[25] R. J. Elliot, I. G. Mathews, and E. W. J. Mitchell, Phil. Mag. **3**, 360 (1958).

rounding edges of the crystals were painted black and covered with thin metal plates in order to avoid the internal effect causing false polarization as mentioned above.

b. Instrumentation and experimental arrangements. As the characteristic excitation light which is essential in the polarization measurements, the 365-mμ light from a 100-W high-pressure mercury lamp was used with an appropriate set of filters. As the host excitation, the 315-mμ light from the same mercury lamp was selected by means of an appropriate combination of filters. Also, saturated solutions of $CoSO_4$ and $NiSO_4$ filling a quartz cell were used as filters in order to remove completely any 365-mμ light from the 315 mμ light. Excitation lights of varying wavelength used in the measurement of polarization spectra were obtained from a 250-mm Bausch & Lomb grating monochromator equipped with a dc-operated 500-W high-pressure xenon lamp.

The exciting light polarized by a Polacoat film on a quartz plate was incident perpendicularly upon the surface of the sample and the polarization of the luminescence was measured at the opposite surface by a cellulose Polaroid sheet. As the detector, an RCA 6199 photomultiplier tube of a head-on type was used. The optical assembly was arranged linearly so that no optical anisotropy exists in the system.

The most difficult experimental problem encountered in polarization measurements of luminescence was to completely eliminate the perfectly polarized excitation light from the luminescence. After careful examinations, a combination of a number of color and interference filters were selected. Whether the requirement is satisfactorily fulfilled or not can be checked by interchanging several filters which attenuate the ultraviolet light from the back to the front of the sample. If the photoresponse of the detector is decreased to negligible magnitude under the same excitation, it is ascertained that we are certainly observing the luminescence excited by the incident ultraviolet light, and that the mixing of transmitted excitation light and of some weak fluorescences emitted by filters is negligible.

c. Procedures of polarization measurements. The polarization of the luminescence was measured for each direction θ of exciting electric vector with respect to a particular crystal axis, and the results were expressed by the conventional definition for the degree of polarization of fluorescence $P_F(\theta)$, given by

$$P_F(\theta)=\left[\frac{I_F(\|)-I_F(\perp)}{I_F(\|)+I_F(\perp)}\right]_\theta, \tag{2}$$

where $I_F(\|)$ and $I_F(\perp)$ are fluorescence intensities with electric vectors parallel and perpendicular, respectively, to the exciting **E** vector. For a given crystal plane, the azimuthal dependences of the P_F of the self-activated blue fluorescence were obtained for both the characteristic and the host excitations as reported in the previous paper.[10]

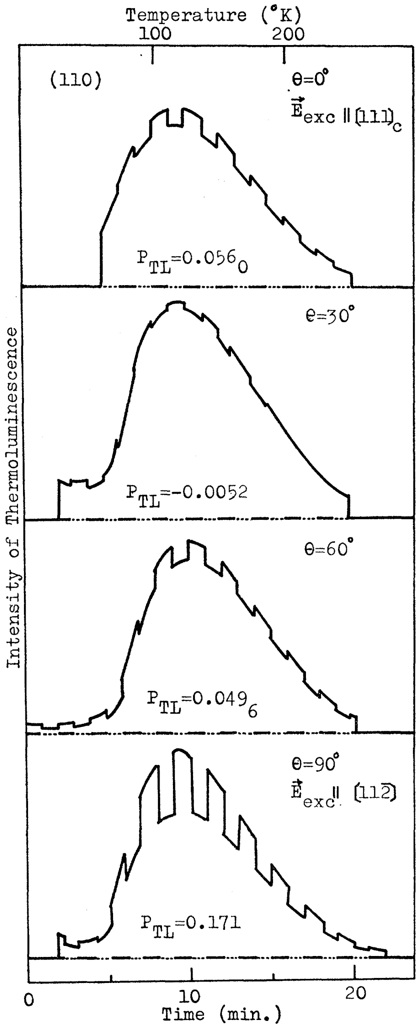

FIG. 5. Polarizations of the thermoluminescence observed at the $(1\bar{1}0)$ plane after excitation by polarized 365-mμ light at 77°K. Angle θ represents the direction of the exciting **E** vector relative to the $[111]_c$ axis. The optical axis of the analyzer was rotated to be parallel or perpendicular, respectively, to the exciting **E** vector alternately in the periods shown by the solid and broken lines.

Thermoluminescence, which was observed after the sample had been excited by the polarized ultraviolet light at 77°K, was found to be polarized, and what was most interesting was that its polarization showed a marked azimuthal dependence when characteristic excitation light was used. A typical example is shown in Fig. 5. The polarization of the thermoluminescence was measured by the same way as that for fluorescence. Also, the degree of polarization of the thermoluminescence P_{TL} was calculated by the same definition as Eq. (2), but here polarized components of thermoluminescence $I_{TL}(\|)$ and $I_{TL}(\perp)$, measured at the glow maximum, were used instead of $I_F(\|)$ and $I_F(\perp)$,

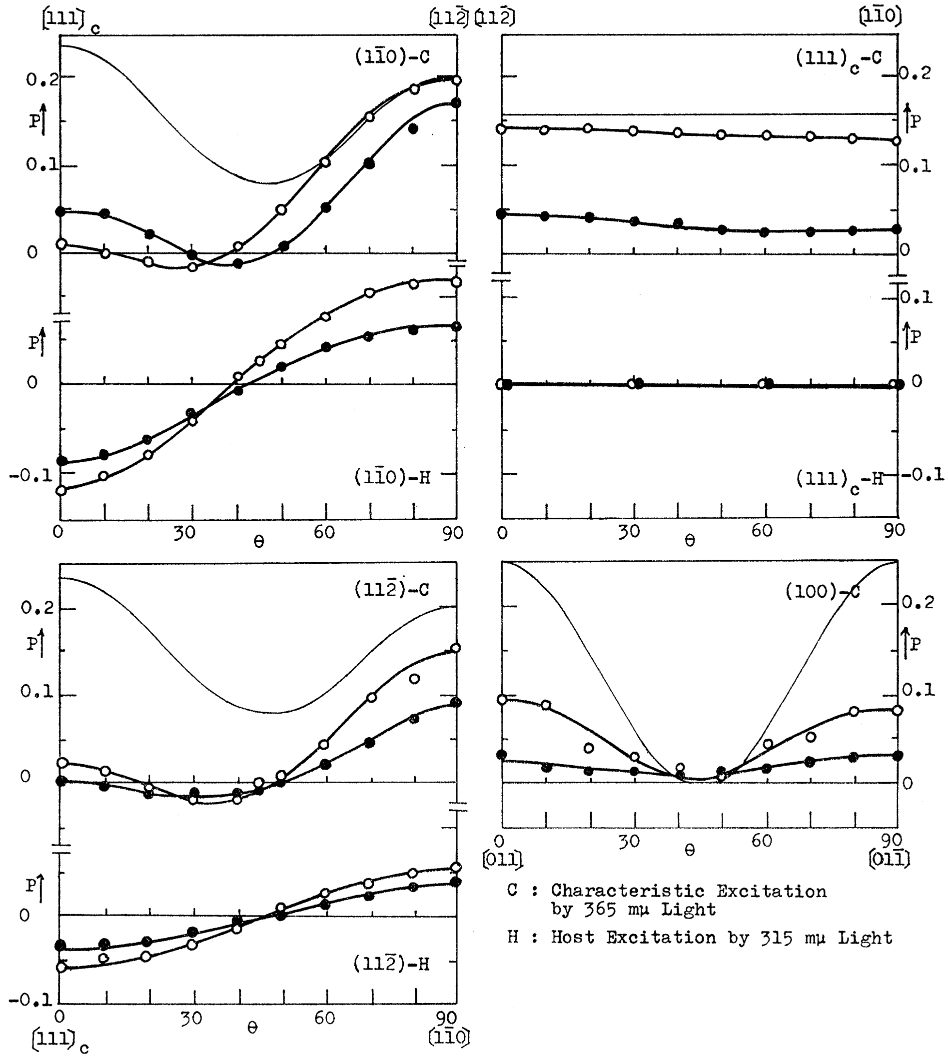

FIG. 6. The azimuthal dependences of the degree of polarization of $P(\theta)$ for the self-activated luminescence in cubic ZnS:Cl single crystal by the characteristic (365-mμ) and the host (315-mμ) excitations. Open circles represent observed P values for the fluorescence at 77°K, while filled circles represent those for the thermoluminescence at about 110°K. Curves drawn by thin solid lines are those calculated for the ⟨111⟩ σ electric dipole model, see Sec. IV in the text.

respectively, in the definition. Thus, the azimuthal dependences of P_{TL} were measured by both the characteristic and host excitations in the same manner as for the fluorescence.

3. Results of Polarization Measurements

a. Azimuthal dependences of the polarization. $P(\theta)$ curves of both fluorescence and thermoluminescence observed for various crystal planes by the two type of polarized light excitations, i.e., the host and the characteristic excitations, are assembled in Fig. 6. Curves drawn by thin solid lines are those calculated by an electric dipole model as will be presented later.

All of the $P(\theta)$ curves for the host excitation indicate that the luminescences are polarized along the direction perpendicular to the $[111]_c$ axis regardless of the direction of the exciting **E** vector. If unpolarized excitation was employed, almost the same $P(\theta)$ curves were obtained for both the host and the characteristic excitations. Such polarizations similar to those observed in hexagonal sulfide crystals[19,20] will be referred as the "spontaneous polarization" in the following descriptions. As reported by Lempicki[20] in some hexagonal and faulted cubic ZnS crystals, the luminescence shows no spontaneous polarization when observed at the plane $(111)_c$ which is perpendicular to the $[111]_c$ axis, as shown in the figure.

On the other hand, $P(\theta)$ curves for polarized characteristic excitation show remarkable azimuthal dependences on the exciting E vectors. The fact that polarization much larger than the experimental errors is observed at the $(111)_c$ plane clearly shows, together with the characteristic azimuthal dependence of the $P(\theta)$ curves, that these polarizations are not due to any dichroic effect of the host lattice.

Finally, in order to investigate the effect of temperature on the polarization characteristics, measurements were carried out at various temperatures, i.e., at 4, 77, 193, and 300°K. The results for the (1$\bar{1}$0) plane are shown in Fig. 7.

b. Polarization spectra. From the classical point of view, polarized light excitation of different wavelength may cause the excitation of other oscillators which have different dipole axes relative to the oscillator responsible for the luminescence. With this hope, the polarization spectra for both the fluorescence and thermoluminescence were investigated in a wide spectral range of the exciting light. In the measurements, the polarization of the emissions by the exciting **E** vector directed along a particular crystal axis was measured as a function of exciting light wavelength. Such spectra were measured at the $(111)_c$ plane for fluorescence and at the (110) plane for thermoluminescence.

The results are shown in Fig. 8, together with the excitation spectra in order to see possible correspondence between two spectra. The dashed line in the polarization spectrum for the (1$\bar{1}$0) plane represents the contribution of spontaneous polarization of the luminescence.

One may immediately find that both the polarization spectra are composed of two bands, one with a maximum at around 363 mμ and the other with a minimum at about 330 mμ. The former band is evidently correlated with the characteristic band observed in the excitation spectra for fluorescence, while for the latter band giving rise to negative P values, one finds no corresponding band in the excitation spectra. In the following descriptions, these two bands found at about 363 mμ and 330 mμ in the polarization spectra will be designated as the first- and the second-characteristic band, respectively.

The advantage of observing polarized thermoluminescence in the measurement of polarization spectra may be worth being mentioned here. Since excitation light through a monochromator is usually weak, polarization measurements for the fluorescence are very difficult and apt to include errors. The thermoluminescence, on the other hand, does not decrease much in intensity even for very weak excitation light, if irradiation of long duration is made. Hence, the polarization spectrum for the thermoluminescence could be extended as seen in Fig. 8, to longer wavelengths where polarization measurement of the fluorescence was impossible due to the mixing of the exciting light.

Attempts have also been made to investigate the effect of the superposition of polarized infrared light on the luminescence. It would be hoped that if the quenching process by infrared irradiation would be due to the optical transition of holes from the ionized luminescence center to the valence band as assumed in the previous discussion, some preferential quenching would be expected to occur due to the polarized infrared light, resulting in a change of polarization of luminescence. Although some changes in the polarization were observed, the results were not so reliable as to permit definite conclusions.

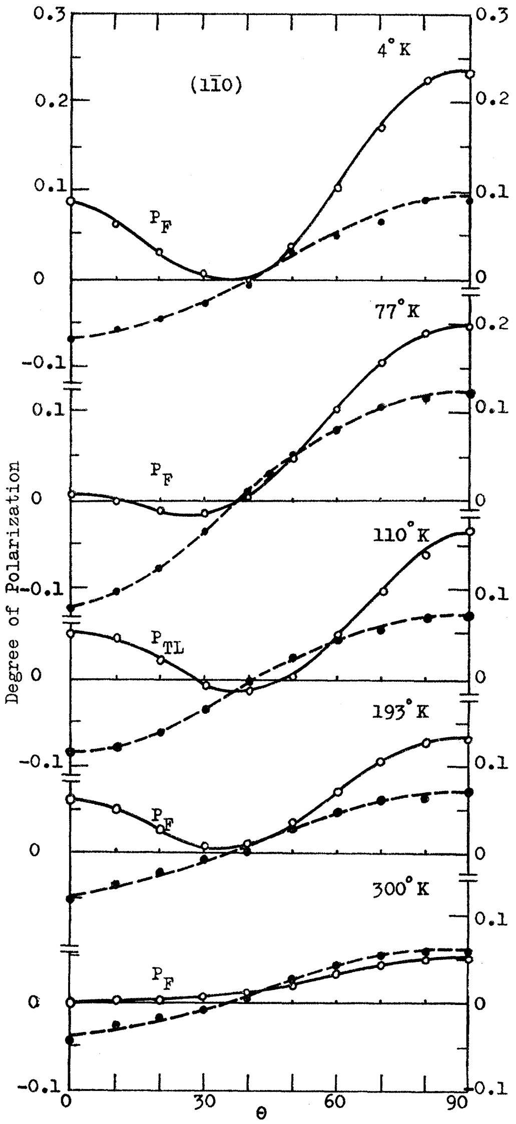

FIG. 7. Temperature dependences of the $P(\theta)$ curves for the (1$\bar{1}$0) plane. Open circles on the solid lines represent the observed P values for the characteristic (365-mμ) excitation, and filled circles on the broken lines represent those for the host (315-mμ) excitation.

The results of the polarization measurements presented in this section lead to the definite conclusion that no matter what the cause of the spontaneous polarization of the luminescence is, the observed characteristic polarization should be attributed to the optical anisotropy inherent in the luminescence center itself. Analysis and discussions of the results will be given in the next section.

IV. DISCUSSIONS ON THE NATURE OF THE LUMINESCENCE CENTER

In the preceding sections, a number of experimental facts has been presented which indicates that the

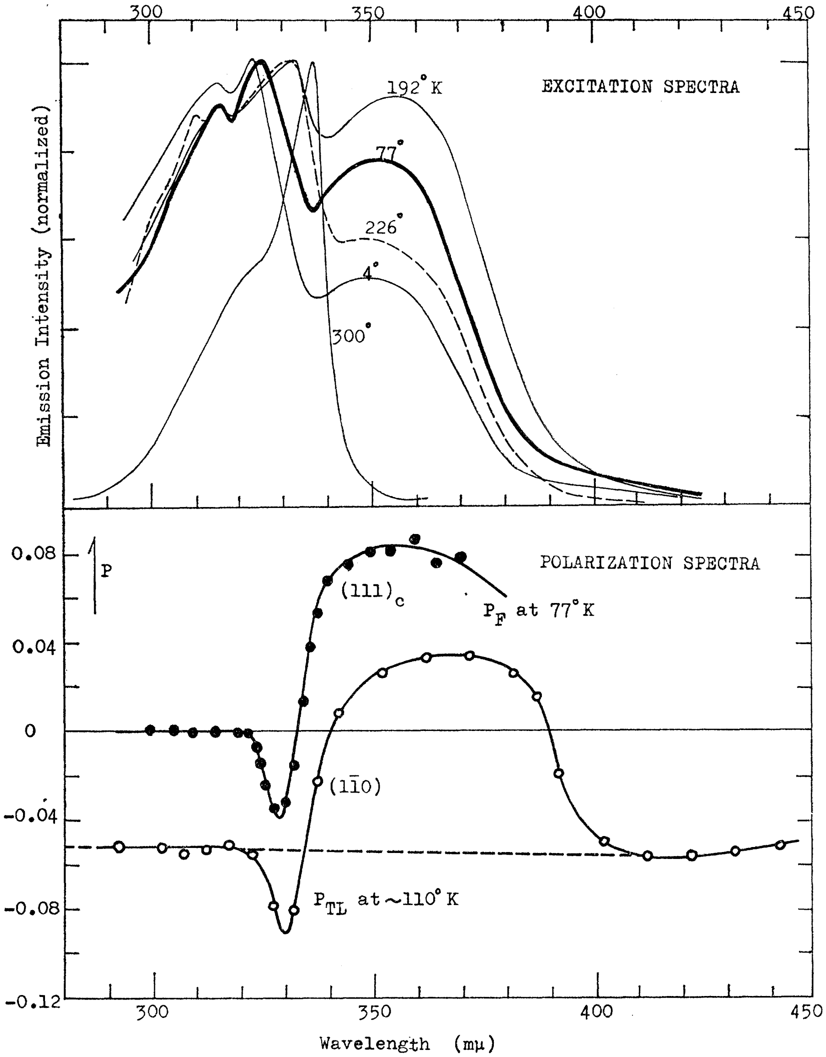

FIG. 8. Excitation and polarization spectra of the self-activated luminescence of cubic ZnS:Cl. Excitation spectra for the fluorescence are given for various temperatures. Polarization spectrum for the fluorescence at 77°K was measured at the $(111)_c$ plane with the exciting **E** vector directed along the $[11\bar{2}]$ axis, while polarization spectrum for the thermoluminescence was measured at the $(1\bar{1}0)$ plane with exciting **E** vector along the $[111]_c$ direction. Dashed line in the latter spectrum represents the contribution of the spontaneous polarization in the direction perpendicular to the $[111]_c$ axis.

electronic transitions involved in the self-activated blue luminescence are localized within the luminescence center. Among these facts, the characteristic polarizations of the luminescence observed have given direct evidence for the conclusion that the center has an axial symmetry within the cubic lattice of ZnS, as will be analyzed in the following section. The next problem aimed at is to clarify the connection between the observed optical anisotropy and the structure of the luminescence center, and thereby to get information about the atomic origin of the electronic states participating in the luminescence process.

1. Classical Electrical Dipole Model

a. Assignment of the ⟨111⟩ electric dipole to the luminescence center. It would be natural to assume an elementary electric oscillator for the luminescence center in the analysis of the characteristic behavior of the polarized luminescence. Such an oscillator will be oriented along one of the symmetry axes in the site symmetries of T_d, C_{3v}, C_{2v}, and C_s in the cubic lattice of ZnS. Each of them has several equivalent directions and oscillating dipoles will be distributed among these equivalent directions. As the first approximation, one may assume that they are populated with equal numbers in these possible orientations. Modification made by taking the possible difference in the population into account will be considered hereafter.

In order to obtain the total polarization of radiation emitted from the crystal by polarized light excitation, one has to sum up the contribution from each of the elementary radiators having different orientations within the crystal. Such calculations have been carried out by Elliot *et al.*[25] for cubic host lattices and general formulas were given in convenient form for both linear and circular electric oscillators. However, in the application of these formulas for faulted cubic ZnS, one has to take into account that the lattices on both sides of the fault plane are twinned with each other, and, therefore, that the numbers of equivalent directions are duplicated except that along the $[111]_c$ axis.

Azimuthal dependences of the degree of polarization of the luminescence were calculated for each of the axial symmetries possible in the faulted zincblende lattice assuming π or σ electric oscillators, and were compared with the observed behaviors of P curves. Here, by π or σ oscillator is meant a dipole in which charge is oscillating linearly along the dipole axis or circulating around it, respectively. Such examinations have led us to the conclusion that the luminescence centers are regarded as σ electric dipoles oriented along the $\langle 111 \rangle$ axis in the cubic ZnS lattice, as reported previously.[10] Curves drawn by thin solid lines in Fig. 6 represent $P(\theta)$ curves calculated for the $\langle 111 \rangle$ σ electric dipole in the faulted cubic lattice of ZnS.

Although the conclusion of the $\langle 111 \rangle$ axial symmetry is unambiguous, the assignment of σ dipole for the center involves some problems. Since the azimuthal behaviors are qualitatively similar to each other for both π and σ dipoles with the same directional distributions, one must examine absolute magnitude of the P values.

As is usual in the polarization studies of luminescence, the calculated magnitude of the P values from the dipole model indicates only the upper limit of the values, and the observed values of P can be smaller than those calculated because of a number of reasons. There may be two possibilities, aside from the effect of the stacking fault which will be discussed later, which give rise to the depolarization of the luminescence in the present case. One of them is thermal depolarization accompanied by the quenching process due to thermal excitation of holes from the ionized luminescence centers as discussed in the previous section. In the luminescence emitted by the subsequent recapturing of these free holes at other luminescence centers, the original memory of the preferential excitation will be entirely lost. Likewise, in the other possibilities luminescence caused by a partial absorption of the incident photons in the host lattice will have no or little polarization, giving rise to an apparent depolarization in the observed luminescence as a whole. The latter mechanism will be dominant at low temperatures where thermal depolarizations due to the former process and to other thermal agitation effects are negligible.

Even if one takes all of these depolarization effects into consideration, however, it is highly unlikely that the original polarization may be ascribed to the π-dipole model which gives P values more than three times larger than those for the σ dipole model.[10] Consequently, the luminescence center has been identified as σ dipole oriented along the $\langle 111 \rangle$ axis as described in the previous paper.[10]

The dipole orientations of the $\langle 111 \rangle$ directions concluded above are along the tetrahedral bonds in the lattice of cubic ZnS. This conclusion, therefore, provides a strong support for the pair model, since the zinc ion vacancy and substitutional halide ion, which are attributed to the pair components in the Prener-Williams model,[6] will be associated at the both ends of the tetrahedral bond in ZnS lattice. The agreement of the symmetry concluded in both paramagnetic and optical studies can be regarded as a further support for the identification of the A center in the ESR absorption spectrum as the luminescence center. However, the most direct evidence for this will be provided by the characteristic polarization of the thermoluminescence presented above.

It will be quite easy to give reasonable explanation for the origin of the polarized thermoluminescence. Under the polarized light excitation in the characteristic band, dipoles having different orientations will experience preferential ionization with a help of thermal activation or by autoionization as discussed in the previous section. The thermoluminescence emitted by subsequent recombination will reveal the memory of the preferential excitation as observed, provided the holes remain in the original luminescence centers. Now, since the appearance of the thermoluminescence is accompanied by the simultaneous decrease of the A signal in the ESR spectrum, both having the same anisotropy, it may be concluded that the centers responsible for both effects are identical.

The electronic transition involved in the excitation of the first characteristic band and that in the luminescence is thus ascribed to the same $\langle 111 \rangle$ σ dipole.

Then the simplest explanation for the second characteristic excitation giving rise to negative P values will be that the transition involved in this excitation is ascribed to the dipole oriented perpendicularly to the radiating dipole. Since the radiating dipole has been assumed to be a σ dipole, this dipole should be assigned as π dipole fixed in the same center. Further discussions about these dipoles will be given in Sec. VI. 2.

b. Possible causes for spontaneous polarization. Since the host lattice of zincblende ZnS is isotropic, there should be no spontaneous polarization in the luminescence if the dipoles are distributed isotropically within the perfectly cubic lattice. For the observed spontaneous polarization which cannot be accounted for by such a simple model as assumed in the preceding section, one may consider two possibilities, i.e., one due to the possible anisotropic effect of the stacking disorder, and the other due to the unequal population of the dipoles.

The sequences of the lattice planes near the stacking fault plane can be regarded as the local wurtzite lattice, and the electric double layer induced in the distorted region will exert an uniaxial electric potential on the lattice in the neighborhood of the stacking fault.[26] The reduction of the site symmetries in the lattice caused by the influence of this potential may also affect the electric oscillators involved in the luminescence

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[26] J. L. Birman, Phys. Rev. **115**, 1493 (1959).

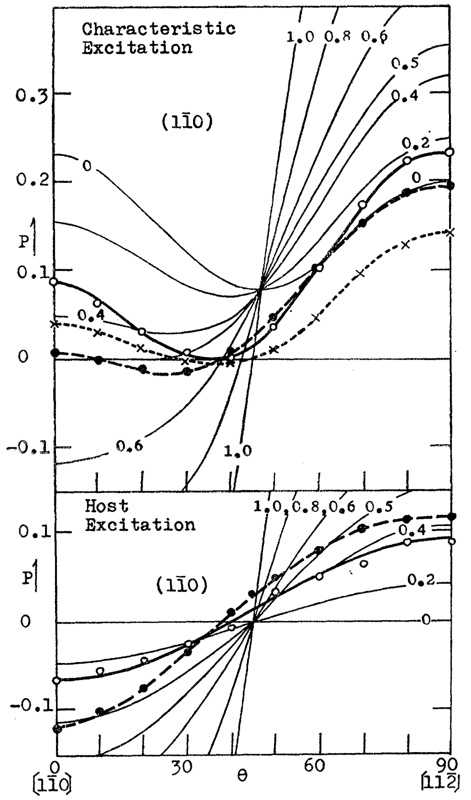

FIG. 9. Modified $P(\theta)$ curves at the $(1\bar{1}0)$ plane calculated for an unequal population of the dipoles. Parameters shown in the figure mean the fraction of the extra $[111]_c$ dipoles in the isotropically populated $\langle 111\rangle$ dipoles. Open and filled circles represent, respectively, the observed P values at 4 and 77°K. Crosses in the figure for the characteristic excitation represent the P values measured after the same sample was annealed at 800°C for 2 h.

center. This possibility will be discussed in the next section.

There will be also another possibility causing the spontaneous polarization. When the dipoles responsible for the luminescence are formed during crystal growth, it may happen that the diffusion mechanism involved in the dipole formation will give rise to unequal population of the dipoles over the equivalent orientations because of large temperature gradient along the crystal growth direction. Since the direction of crystal growth in ZnS is usually parallel to the $[111]_c$ axis (this means that the stacking fault planes are introduced to be parallel to the growing surface), this possibility will also result in the preferential polarization of luminescence relative to the $[111]_c$ axis.

One will be able, at any rate, to describe the effects of both possibilities phenomenologically by introducing dipoles oriented along the $[111]_c$ axis in excess or in deficiency to the isotropic population. Taking the amount of such extra dipoles as a parameter, one can calculate the modified $P(\theta)$ curves as shown in Fig. 9. Likewise, taking account of the depolarization as the second parameter, observed $P(\theta)$ curves shown in Figs. 6 and 7 could be reproduced almost exactly by the suitable adjustment of these two parameters, indicating that one can understand quantitatively both of the characteristic and spontaneous polarizations of the luminescence of a given crystal by the modified dipole model considered above. But due to the lack of knowledge for the complicated mechanisms involved, the adopted values for these parameters can be hardly correlated at present with certain quantities with physical meaning. The results of electron-spin-resonance measurements showed that the line in the A signal corresponding to the $[111]_c$ spin is stronger than others in the crystals used here,[9] but the quantitative estimation of each population was not successful because of several experimental difficulties.

An attempt to see whether the spontaneous polarization is affected by thermal treatment was done by annealing the crystal at 800°C for 2 h in an atmosphere of argon gas. The two $P(\theta)$ curves for the $(1\bar{1}0)$ plane observed before and after the annealing, respectively, are shown in Fig. 9. The change of the curves by the annealing seems to show some tendency toward the more isotropic population of the dipoles after the treatment.

2. Atomic Structure of the Luminescence Center

a. Selection rules for the luminescence center. The symmetry axis of the dipole which has been assigned to the luminescence center lies along one of the tetrahedral bond directions in the cubic ZnS lattice. Then, covalent bonds surrounding the dipole will give the axial symmetry of C_{3v} to the center, and each energy state involved in the center should belong to one of the irreducible representations, A_1, A_2, or E of C_{3v} group, if a possible spin-orbit interaction is neglected. Group theory shows that optical transitions are allowed in $A_1 \leftrightarrow A_1$ and $A_1 \leftrightarrow E_1$, respectively, for linearly polarized light along the dipole axis and for circularly polarized light around the axis. In other words, these transitions are regarded classically as π and σ dipoles, respectively, both being oriented along the $\langle 111\rangle$ axis.

According to these arguements, the assignments of dipoles concluded in the preceding section can be interpreted in terms of the group theoretical expressions as follows: The transition responsible both for the luminescence and for the first characteristic excitation, which was ascribed to σ dipole, corresponds to $A_1 \leftrightarrow E$ transition, while the second characteristic excitation to which π dipole was assigned, corresponds to $A_1 \leftrightarrow A_1$ transition within the luminescence center having C_{3v} symmetry. Consequently, the ground state of the center is concluded to be the A_1 state participating in both transitions. This is quite reasonable since the A_1 state corresponds to that with no orbital angular momentum. Thus, the two excited states found in the polarization spectra are assigned to the E and A_1

states, respectively. According to the arguments presented in the previous section, the excitation of the center into the higher excited state A_1 is followed by the nonradiative transition to the lowest excited state E, from which subsequent transition to the ground state A_1 takes place giving rise to the luminescence. These assignments of the states are shown in Fig. 4 presented before.

Some inference may be made here about the effect of the stacking faults on the energy states in the luminescence center. In the vicinity of the faulted region, the symmetry of the center, except that oriented along the $[111]_c$ axis, will be reduced from C_{3v} to C_s by the unidirectional electrostatic potential along the $[111]_c$ axis as discussed before. Twofold degeneracy in the E state, then, suffers Stark splitting into the A' and A'' states belonging to C_s group, likewise the A_1 state changes to the A' state.[27] Selection rules between these levels are also given by group theory to be that $A' \leftrightarrow A''$ transition is allowed for electric vector perpendicular to the mirror plane, while $A' \leftrightarrow A'$ transition is allowed for electric vector lying in the plane. We have no experimental data at present for determining which of these states split from the E state corresponds to the lowest excited state in the distorted center, but the tentative assumption that the A'' state is lower will be made in the next subsection to explain the temperature dependence of the polarization.

b. Physical pictures of the energy levels. Although one has no direct experimental evidence yet that chlorine ion incorporated in the crystal is surely participating in the luminescence center,[28] there are a number of experimental facts in favor of the association model proposed by Prener and Williams.[6] In this model, a zinc-ion vacancy is surrounded by three sulfur ions and a chlorine ion at tetrahedral corners. One may roughly approximate this center as a four-atomic molecule, as shown in Fig. 10, imbedded within the dielectric continuum of cubic ZnS lattice. In the ground state, each of three hybridized bond orbitals protruding from the three sulfur ions toward the zinc-ion vacancy is filled with a pair of electrons, while the associated chlorine ion has completely closed shells. Since the substitutional chlorine ion bears effective charge of $+e$, it will be able to accommodate an additional electron in the $4s$ orbital outside the inert core.

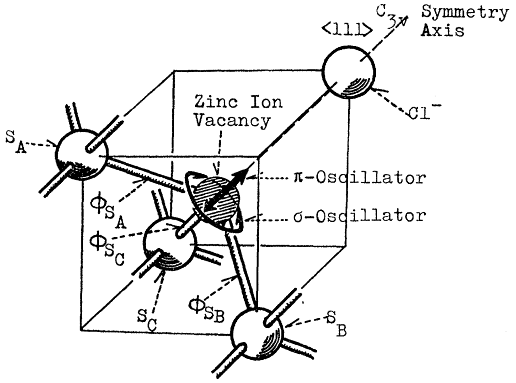

FIG. 10. The association model for the self-activated luminescence center in cubic ZnS:Cl crystal. Regarding the notations given in the figure, see the text.

Let the three bond orbitals directed toward the zinc-ion vacancy from the three sulfur ions S_A, S_B, and S_C be ϕs_A, ϕs_B, and ϕs_C, respectively, and the $4s$ orbital of the chlorine ion by ϕ_{Cl} (refer to Fig. 10). In the simple LCAO approximation, a set of four symmetry functions corresponding to the irreducible representations of C_{3v} group is constructed from the atomic orbitals presented above as follows:

$$\begin{aligned}
\Phi_1(a_1) &= (1/\sqrt{3})[\phi\, s_A + \phi\, s_B + \phi\, s_C],\\
\Phi_2(a_1) &= \phi_{Cl}, \qquad\qquad\qquad\qquad\qquad\qquad\qquad (3)\\
\Phi_{3,4}(e) &= (1/\sqrt{3})[\phi\, s_A + \exp(\pm 2\pi i/3)\cdot\phi\, s_B\\
&\qquad\qquad + \exp(\pm 4\pi i/3)\cdot\phi\, s_C].
\end{aligned}$$

Both functions Φ_1 and Φ_2 have A_1 symmetry (a_1 orbitals), while Φ_3 and Φ_4 belong to a doubly degenerate state (e orbital) E.

Physical pictures for these orbitals may be described as follows: Electron (or hole) in the orbital expressed by Φ_1 is stationary shared among the three bond orbitals of sulfur ions, while in the doubly degenerate Φ_3 and Φ_4 orbitals electron (or hole) is rotating among the bonds due to resonance in either direction of the rotation around the symmetry axis of the center. The orbital Φ_2 means the trapping of an electron at the chlorine ion with an effective charge of $+e$.

In order to set up the energy level scheme of the luminescence center with this approximation, one has to deal with six electrons originally existing in the three sulfur-bond orbitals. In the ground state of the center, they will be all accommodated on Φ_1, Φ_3, and Φ_4 orbitals according to Pauli's principle, and the resultant state will be ${}^1A_1$. When the center is subjected to excitation, one of these electrons will be transferred onto the halide ion, leaving a hole behind. Then, there will result two excited states, depending on the orbital on which the hole is located. The resultant state will be A_1 if the hole is on the Φ_1 orbital, while it will correspond to the E state if the hole is accommodated in the orbital represented by Φ_3 or Φ_4.

According to the discussion given in the previous section, one may immediately correlate these pictures with the observed optical transitions in the luminescence center. The first excited state E is brought about by the absorption of light polarized in the plane perpendicular to the symmetry axis, and is interpreted to be that an

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[27] The similar situation for the luminescence center in SiC crystal was treated by L. Patrick, Phys. Rev. **117**, 1439 (1960).

[28] Although Kasai and Otomo (in Ref. 8) attributed the observed difference in the linewidths of A signals between ZnS coactivated by Cl, and that by Br to the unresolved hyperfine interaction with the halide ion, an alternative explanation for this was presented recently by Schneider *et al.* (Ref. 29).

electron on sulfur ions is transferred to the halogen ion and the hole left behind is rotating around the symmetry axis among the three sulfur bond orbitals. Consequently, the luminescence emitted when the electron returns back and recombines with the hole is also polarized circularly around the symmetry axis. On the other hand, in the second excited state A_1 which is caused by the light excitation linearly polarized along the axis, the hole is stationary localized in the sulfur bonds.

So far, these levels have been all considered as spin-singlets. There will also be a possibility for the triplet states with parallel spins of the electron and the hole to exist. A metastable state which was found to be located about 0.01 eV below the emitting state and to be responsible for the temperature-dependent slow exponential component in the decay of the luminescence[17] might correspond to one of these triplet states.

When the excited electron is ionized from the chlorine ion, the spin of the hole makes the center paramagnetic. The g values of such a hole were calculated by Kasai and Otomo[8] with a molecular orbital treatment similar to that given above using the same function as Φ_1 instead of $\Phi_{3,4}$ which is assumed for the hole in the ionized center here, resulting in fair agreement with the observed g values. However, the calculated g values by the two alternative treatments, assuming Φ_1 or $\Phi_{3,4}$ for the hole do not differ so much as to permit one to decide which model is correct, if the overlappings between neighboring sulfur bonds are small.

On the other hand, Schneider and his collaborators[29] recently performed ESR measurements for ZnS:Cl crystal at very low temperatures, and found that the axial symmetry of the g tensor corresponding to the A signal at 77°K is reduced to orthorhombic symmetry at lower temperatures. They explained this in terms of the localization of the hole at one of the sulfur ions surrounding the vacancy. According to their explanation, the hole localized in the ionized luminescence center is frozen in one of the bond orbitals of sulfur ions at very low temperatures, giving rise to a slight distortion of the center and consequently, to g tensor of the orthorhombic symmetry. When the temperature is raised, this fixed hole begins hopping between the three equivalent bond orbitals of sulfur, and at 77°K this hopping motion of the hole around the pair axis reaches so high a frequency that averaged in time, it will give rise to the axially symmetric g tensor. Although Schneider *et al.* considered that the distortion in the center still remains instantaneously at liquid nitrogen temperature, the hole hopping among the sulfur bonds will appear as a σ electric dipole at elevated temperatures, in good accord with the present model.

Because of the orbital degeneracy of the E state which is assigned to the lowest excited state, one might expect Jahn-Teller distortion to take place in the excited luminescence center as observed in the g values. Aiming at the detection of the effect of such a distortion on the polarization characteristics of the luminescence, polarization measurements were performed at liquid helium temperature. Results were already shown in Fig. 7. Although no remarkable change of $P(\theta)$ curve was observed when temperature was decreased from 77 to 4°K, one may notice some anomalies in the temperature dependence of the P values for the $[111]_c$ direction. Namely, with lowering temperature from about 200°K, the degree of polarization by the characteristic excitation decreases, reaches a minimum at around 50°K, and then increases. On the other hand, the spontaneous polarization by the host excitation shows a maximum at the same temperature. Such a behavior observed for several samples was more remarkable for the crystal which contains a larger amount of the stacking faults.

A plausible speculation involving the possible effect of the Jahn-Teller distortion at very low temperatures, and of the stacking disorders on the luminescence center, will be given as follows: Since the magnitude of the P values for the $[111]_c$ direction at 77°K depends on the amount of stacking faults in the sample, the first decrease of the polarization with lowering temperature will be related to the influence of the stacking disorder on the luminescence center located nearby. The reduction of the symmetry of the center form C_{3v} to C_s due to the field of the fault gives rise to splitting of the two-dimensional state E into the A' and A'' levels, as discussed before. Here, let us tentatively assume the lowest excited state in these C_s centers to be the A'' state as shown in Fig. 4. At elevated temperatures where thermal energy becomes comparable or superior to the electrostatic potential energy due to the stacking fault, the luminescence emitted from these centers will have little preferential polarization. As temperature is decreased, however, the excited state will be frozen in the A'' state and the luminescence emitted by the transition to the ground state A' will be preferentially polarized perpendicularly to the mirror plane, and hence also to the $[111]_c$ axis, resulting in the decrease of the P value for the $[111]_c$ direction. By further decrease in temperature, the other centers remote from the faulted region will be subjected also to the reduction of symmetry to C_s by the Jahn-Teller distortion. After the distortion, the dipole responsible for the luminescence changes from a circulating oscillator to a linear oscillator directed randomly within the lattice. Thus, the preferential polarization perpendicular to the $[111]_c$ axis will be made less prominent again.

It will need further experimental efforts to investigate the effect of Jahn-Teller distortion speculated above.

V. SUMMARY OF THE CONCLUSIONS AND FINAL REMARKS

Among several results presented in this work, the following, summarized below, are important to clarify the nature of the self-activated blue luminescence center in ZnS:

(1) The luminescence center has an axial symmetry directed along the ⟨111⟩ axis which is parallel to the tetrahedral bond in the cubic ZnS lattice.

(2) The anisotropy observed in the thermoluminescence, which appears at the expense of the A signal in the ESR absorption spectrum, provides the direct evidence for the identification of the spin center with the luminescence center.

(3) There have been found two characteristic bands in the polarization spectra. They are attributed, respectively, to the π and σ dipoles fixed in the same luminescence center. The luminescence is due to the same σ dipole.

(4) Quantum mechanically, the ground state of the center is assigned to that with A_1 symmetry of the C_{3v} group, while the two excited states are to the E and A_1 states, respectively. According to the selection rules between these levels, the lowest excited state from which the luminescence transition takes place is ascribed to the E state.

(5) Physical pictures for these levels are given on the basis of the association model of a zinc-ion vacancy with a chlorine ion as proposed by Prener and Williams. In the excited state E, one electron excited from the sulfur ions surrounding the vacancy resides in the $4s$ orbital of the chlorine ion, and the hole left behind is supposed to be rotating among the three equivalent sulfur ions around the pair axis. This picture seems to be quite consistent with the observed behavior of the spin center reported recently by Schneider *et al.*[29]

Among the problems left for the further investigation, complicated effects due to the stacking disorder on the luminescence center will be the most important one for the quantitative analysis of the polarization characteristics. When it is achieved, the possible effect of the Jahn-Teller distortion of the center will be made clearer. Not only for the self-activated luminescence, but for the most of luminescences in cubic crystals, the investigation of the Jahn-Teller effect will be able to provide valuable information on the energy states participating in the luminescence.[30]

Regarding the study about the self-activated luminescence center in ZnS crystal, we do not yet have definite evidence that coactivator ions incorporated are surely associated with the zinc-ion vacancy in the center. It is hoped that measurements by means of the ENDOR technique may be carried out to settle this problem.

Polarization measurements similar to those reported here will be one of the most useful methods for the study of other kinds of luminescence centers in ZnS type crystals. Measurements of the self-activated luminescence of ZnS single crystals coactivated by VIIb or IIIb group ions other than chlorine ion, and measurements of the luminescence due to usual activator ions are now in progress.

ACKNOWLEDGMENTS

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[29] J. Schneider, W. C. Holton, T. L. Estle, and A. Räuber, Phys. Letters **5**, 312 (1963).

[30] Such efforts for KCl:Tl were done by C. C. Klick and W. D. Compton, Phys. Chem. Solids **7**, 170 (1958); and by H. Kamimura and S. Sugano, J. Phys. Soc. Japan **14**, 1612 (1959).