

Table I. Comparison of theory and experiment.

Sample	D (Å)	Linewidth δH (gauss)	Extra linewidth ^a $\Delta(\Delta H_0)$ (gauss)	Extra broadening Δ	
				(meas)	(calc)
No. 1 (Pb in glass)	~100	10.3	9.4	0.071	0.045
No. 2 (Pb in glass)	~300	5.2	3.0	0.023	0.026
No. 3 (standard)	4×10^4	4.2	0

$$^a \Delta(\Delta H_0) = (\delta H^2 - \delta H_{\text{standard}}^2)^{1/2}.$$

particle resonance line superimposed upon a standard resonance line. The standard line, in each case, was obtained from an equivalent amount of large lead particles distributed over the same volume. Auxiliary measurements determined the natural line width of lead³ to be 4.2 gauss and the Knight shift to be 1.47%.

Examination of the NMR traces indicates that if any deviation of the line position occurs it is too small to be observed. Such a result is in line with expectation. On the other hand, the line broadening is extensive and Table I compares the extra broadening estimated using Eq. (9) with that observed. The correspondence is satisfactory and lends support to the present description of the effect. It is seen that the measured values of Δ do not fully establish an inverse square root dependence on size. We attribute this lack of agreement to uncertainties in assigning characteristic sizes to the lead particles, particularly over the small range investigated.

Since the extra broadening of the resonance line is attributed to a distribution of Knight shifts it should exhibit a magnitude proportional to the field. Experiments at 12, 8, and 6 kG did, in fact, show the observed linewidth to decrease approximately as the ratios 1.7:1.2:1. These values give a roughly linear relationship between extra linewidth and field as required.

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²A. Blandin and E. Daniel, *J. Phys. Chem. Solids* **13**, 257 (1959).

³L. I. Piette and H. E. Weaver [*J. Chem. Phys.* **28**, 735 (1958)] give the linewidth of lead as 2.6 gauss and the Knight shift as 1.4%. While we concur on the value of the shift, we are unable to account for the difference in the linewidths. The presently determined value is used for calculations in this work.

OPTICAL SYMMETRY OF THE SELF-ACTIVATED LUMINESCENCE CENTER IN ZnS SINGLE CRYSTAL

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In the investigation of the nature of luminescence centers, especially the symmetry thereof, the measurement of the polarization of luminescence is a very useful tool. The polarization of luminescence in ZnS type crystals was reported by some investigators.¹ However, the results obtained up to the present were all explained by attributing the polarization to the symmetry of the energy bands of the hexagonal host

lattice.² The polarization which correlates with the symmetry of the luminescence center itself as found in alkali halides³ and diamond⁴ has never been found in sulfide crystals. This is the first report that in ZnS type crystals the optical symmetry of the luminescence center has been revealed by the polarization characteristics, thereby presenting information about the nature of the radiative transition.

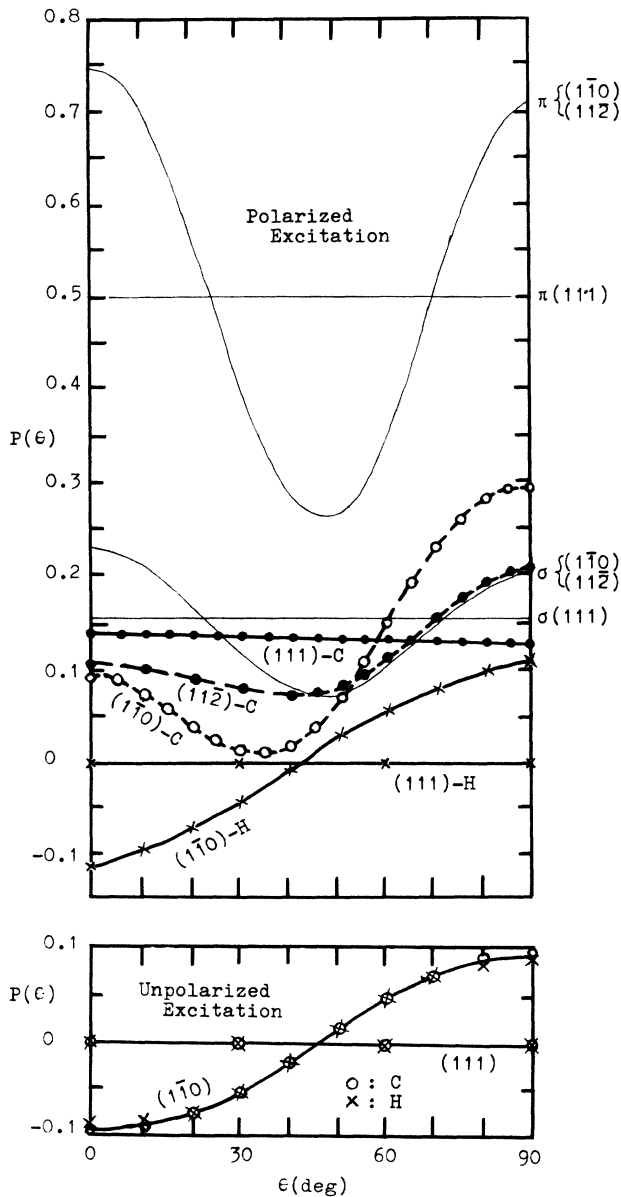


FIG. 1. The degree of polarization $P(\theta)$ for the self-activated luminescence of ZnS single crystal at 77°K . The excitation was with light in the characteristic excitation band (the $365\text{ m}\mu$ mercury line) (denoted by C) as well as in the host crystal excitation band ($340\text{ m}\mu$ monochromatic light) (denoted by H). θ is the angle between the optical axis of the polarizer (or the analyzer in the case of unpolarized excitation) and a particular crystal axis, $[111]$ for the surfaces $(1\bar{1}0)$ and $(11\bar{2})$, and $[11\bar{2}]$ for the surface (111) . Open circles, closed circles, and crosses show the experimental results. Curves drawn with thin solid lines are $P(\theta)$ curves calculated assuming π or σ dipole with the isotropic population among the seven equivalent bond directions.

A ZnS single crystal⁵ grown from the melt⁶ was used. This crystal has the cubic zinc-blende structure with a considerable amount of stacking disorder, in other words, the cubic structure involving a small amount⁷ of hexagonal region. The crystal contains chlorine as a contamination impurity and shows the so-called "self-activated" luminescence with a peak at about $470\text{ m}\mu$ due to chlorine as coactivator.⁸ The excitation spectrum for this luminescence has a characteristic excitation band with a peak at about $360\text{ m}\mu$, which is clearly separated from the fundamental absorption edge of the host crystal.⁸ The crystal was cut and polished to a cubic shape with three mutually perpendicular surfaces, one of which is a cleavage surface. If the c axis in the hexagonal region is defined as the $[111]$ axis, the cleavage surface is the $(1\bar{1}0)$ plane. The other two surfaces are both the polished ones, being nearly parallel to the $(11\bar{2})$ plane (within an error of the angle of 10°) and the (111) plane (within 2°), respectively.

In the polarization measurement, one of the crystal surfaces was irradiated perpendicularly by polarized excitation light, and the polarization was measured for the luminescence emitted from the opposite surface. The results were expressed by the degree of polarization, $P(\theta) = [(I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})]_{\theta}$, where I_{\parallel} and I_{\perp} are the emission intensities measured with the analyzer parallel and perpendicular, respectively, to the polarizer, and θ is the angle between the optical axis of the polarizer and a particular crystal axis. Excitation was with ultraviolet light in the characteristic excitation band (the $365\text{ m}\mu$ mercury line) as well as in the host crystal excitation band ($340\text{ m}\mu$ monochromatic light). $P(\theta)$ curves for unpolarized excitation were also measured. In this case, θ is the angle between the optical axis of the analyzer and the particular crystal axis.

The $P(\theta)$ curves measured at 77°K are shown in Fig. 1. It is noticed that in the case of the characteristic excitation the $P(\theta)$ curves depend remarkably on whether the excitation is polarized or unpolarized, whereas in the case of the host excitation the $P(\theta)$ curves are quite independent of that and are almost the same as those under the unpolarized characteristic excitation. These results are understood, if one assumes that the polarization of the luminescence is caused by the local symmetry properties of the luminescence center. Since the crystal involves a small amount of the hexagonal region, there is the possibility

that the polarization might be due to the symmetry of the valence band of the hexagonal structure.² However, this possibility can be ignored, if one takes into consideration that the polarization characteristics under the characteristic excitation depend on whether the excitation is polarized or unpolarized, and further that the $P(\theta)$ curves under the polarized characteristic excitation cannot be explained if the hexagonal effect mentioned above is assumed. The results under the host excitation are understood, if it is considered that since this excitation is followed by the migration of free carriers, the polarization of the luminescence in this case depends only on the emission process. From these arguments, one can conclude that the self-activated luminescence center has its own characteristic symmetry properties.

Based on this conclusion, the observed anisotropy of the luminescence can be explained by the following arguments. Prener and Williams⁹ proposed that the self-activated luminescence center is a zinc vacancy, in which both of the two holes are ionized, with one of its charge-compensating halogen ions associated at one of the nearest sulfur sites. Recently, Kasai and Otomo¹⁰ found a photosensitive electron spin resonance absorption with the self-activated ZnS phosphors, and showed that the spin center which they attributed to the self-activated luminescence center has anisotropy consistent with the Prener-Williams model. This type of electron spin resonance (ESR) absorption was also observed with the single crystal used here by the present authors,⁸ and the same results as Kasai and Otomo's were obtained.

According to the Prener-Williams model, the center should have the axial symmetry of C_{3v} . In the center of this symmetry, the ground state presumably belongs to A_1 symmetry, since this symmetry corresponds to the state with zero angular momentum. Optical dipole transitions are allowed between this ground state and the upper excited states A_1 and E . From consideration of the selection rules, the optical transition in this center can be considered classically as π or σ dipole¹¹ oriented along the symmetry axis, the former being for $A_1 \rightarrow A_1$ transition and the latter for $A_1 \rightarrow E$ transition. Such dipole transitions in a crystal with tetrahedral bonds were discussed by Patrick¹² for the polarized edge emission of SiC.

The calculation of $P(\theta)$ curves were performed for such π and σ dipoles assuming equal population of the dipoles among the possible bond di-

rections. In the cubic ZnS lattice with stacking disorder, there are seven equivalent bond directions among which such dipoles can be distributed. The results are shown in Fig. 1. Comparing the $P(\theta)$ curves experimentally observed under the polarized characteristic excitation with those calculated, one may conclude that the observed anisotropy of the luminescence can be explained by the σ dipole considered above.

The polarization of the luminescence observed under the unpolarized characteristic excitation, and also that under the host excitation, cannot be explained by a σ dipole with an isotropic population. These facts may be explained if one assumes either or both of the following two possibilities. One is that the symmetry properties of the valence band of the hexagonal region partly involved in the crystal exert an influence on the local symmetry possessed by the center itself. The other is that the σ dipole is not populated isotropically among the bond directions and the population along the $[111]$ axis, which is the direction of the crystal growth, is larger than that along the other axes. It is very difficult at present to decide which possibility is responsible. An attempt to estimate the population of the center among the different bond directions by ESR measurement was unsuccessful. Whichever is the case, however, the conclusion that the center has its own lower symmetry is not affected.

Based on the above conclusion of the σ dipole for the self-activated luminescence center, one can make the following inference about the nature of the electronic transition responsible for the luminescence. In the ground state of the associated center as suggested by Prener and Williams, the three bond orbitals surrounding the zinc vacancy are all filled with electrons. When excited by light in the characteristic excitation band, one of these electrons will be transferred to the halogen ion in the center, leaving one positive hole in the bond orbitals. This excited hole will rotate around the symmetry axis of the center due to resonance among the three bond orbitals. The luminescence, then, occurs as the reverse process of the excitation. This type of transition can be considered classically as a σ dipole, coinciding with the conclusion obtained above. With the energy band scheme, this transition can be regarded as that which takes place within the associated center of the Prener-Williams model between the acceptorlike level originating from the zinc vacancy and the donorlike level originating from the substitutional halogen ion associated.

More detailed studies on the anisotropy of the self-activated luminescence center, including the polarization of the thermoluminescence associated with the center, are now in progress.

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⁴R. J. Elliott, I. G. Matthews, and E. W. J. Mitchell, *Phil. Mag.* **3**, 360 (1958).

⁵Kindly supplied by Dr. A. Addamiano, General Elec-

tric Co., Cleveland, Ohio.

⁶A. Addamiano and M. Aven, *J. Appl. Phys.* **31**, 36 (1960).

⁷Actually about 10% according to x-ray analysis.

⁸S. Shionoya, T. Koda, K. Era, and H. Fujiwara, *J. Phys. Soc. Japan* **18**, Suppl. II, 299 (1963).

⁹J. S. Prener and F. E. Williams, *J. Chem. Phys.* **25**, 361 (1956).

¹⁰P. H. Kasai and Y. Otomo, *Phys. Rev. Letters* **7**, 17 (1961); *J. Chem. Phys.* **37**, 1263 (1962).

¹¹In the nomenclature used here, π or σ dipole means parallel or perpendicular, respectively, to the symmetry axis of the center. See E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (University Press, Cambridge, 1935), Chap. IV; also reference 12.

¹²L. Patrick, *Phys. Rev.* **117**, 1439 (1960).

JOSEPHSON CURRENTS IN SUPERCONDUCTING TUNNELING: THE EFFECT OF MICROWAVES AND OTHER OBSERVATIONS*

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In the course of experiments on the effect of microwave fields on superconducting tunneling, we have had occasion over the past few months to fabricate many tunneling crossings of low resistance (5-20 Ω with a crossing area of 1.5×10^{-4} cm²). Every one of these samples has exhibited the zero-voltage currents predicted by Josephson¹ and attributed, in effect, to the tunneling of Cooper pairs. The observation of these currents has already been reported by Anderson and Rowell.² Our experiments have brought to light several new effects which we summarize below.

The samples were Al/Al₂O₃/Sn. Two five-mil-wide Al lines, evaporated onto cleaned glass substrates, were oxidized in a glow discharge generated in an atmosphere of about 0.1 Torr of dry oxygen for 15 seconds. A five-mil-wide cross-strip of Sn was then evaporated forming two samples on each substrate.

The tunneling current versus voltage characteristics were displayed on an X-Y oscilloscope. A low-impedance source was used to drive the loop containing the sample and the current-measuring resistor. The latter, and thus the circuit load line, could be varied, either in calibrated steps or continuously, from 10 Ω to 10 000 Ω . The source was either dc, ac, or both in combination. Generally 60-cps ac was used though other frequencies were employed as desired.

No attempt was made to shield the earth's magnetic field. Most data were taken at about 0.9°K.

The following observations were noted in the course of experiments with a large number of tunneling crossings:

1. Using an ac display, Fig. 1 shows for a typical sample the zero-voltage current predicted by Josephson and previously observed with a dc technique by Anderson and Rowell. During each half-cycle of the sweep, current

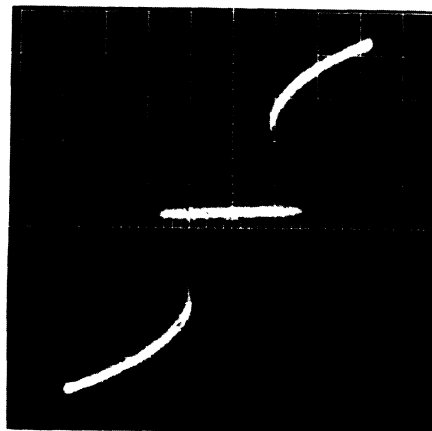


FIG. 1. I - V characteristic near origin showing zero-voltage Josephson current and negative resistance switching trace. Vertical scale 58.8 μ V/cm, horizontal scale 130 nA/cm.