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Mechanism of the Killer Effect of Iron-Group Ions on the Green Luminescence in ZnS:Cu, Al Phosphors

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To investigate the mechanism of the killer effect of iron group ions (M^{2+}) on the green luminescence in ZnS:Cu, Al phosphors, the dependences of the intensity and decay rate of the green luminescence on the M^{2+} concentrations, the relation of the green luminescence intensity vs. excitation intensity, and some other related optical properties are measured. It is concluded, together with some theoretical calculations, that the killer effect of Mn^{2+} ion is mostly due, especially at low temperatures, to the resonance energy transfer. In the cases of Fe^{2+} , Ni^{2+} , and Co^{2+} ions, it is concluded that the killer effect is caused not only by the energy transfer but also by the bypassing process via deep levels created by these ions, and that the effect due to the bypassing process is enhanced with increasing temperature.

§1. Introduction

It is well known that in ZnS type phosphors small amounts of iron group ions involved as impurities remarkably quench the intensity of various kinds of luminescences. This fact has been known for a long time, and called the "killer effect" of iron group ions. The mechanism of this effect has not been clearly understood, however. We have investigated in this paper the mechanism of the killer effect of Mn^{2+} , Fe^{2+} , Ni^{2+} , and Co^{2+} ions (designated as M^{2+} ions) on the well-known green luminescence in ZnS: Cu, Al phosphors.

In II-VI compounds, various kinds of broad-band luminescences are produced by doping acceptor-type activators of Ib elements and donor-type coactivators of VIIb or IIIb elements. Among these luminescences, the green luminescence due to copper activators (usually called the G-Cu luminescence) in ZnS is most widely known. The spectrum of this luminescence is a broad band with a bell shape having a peak at nearly 2.4 eV and a half-width of about 0.3 eV.

The mechanism of this luminescence is now well understood. As a result of the extensive measurements of time-resolved emission spectra and other related luminescence properties performed by one of the authors and his coworkers,¹⁻⁴⁾ it has been concluded that this

luminescence is reasonably explained by the concept of the donor-acceptor pair emission mechanism. Namely, the green luminescence is due to the recombination radiation of electrons and holes trapped at various pairs of copper acceptors (activators) and aluminum donors (coactivators) with diversely different separations. The direct evidence for this conclusion has been presented by the measurements of the relationship between the decay rate of the green luminescence and those of two kinds of photo-induced absorptions, one due to holes created at copper acceptors and the other due to electrons trapped at aluminum donors. The schematic picture of the mechanism of this luminescence is shown in Fig. 1. Electrons excited to the conduction band from the

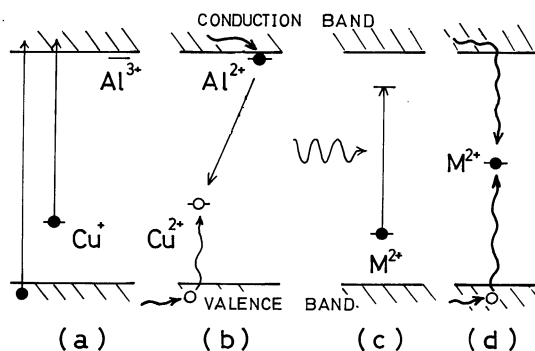


Fig. 1. Schematic pictures of (a and b) the mechanism of the G-Cu luminescence in ZnS: Cu, Al, (c) the killer effect of iron group ions (M^{2+}) due to resonance energy transfer, and (d) the killer effect due to the bypassing process.

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mono-valent copper level or from the valence band by ultraviolet light are captured at the aluminum donor level, and then the green luminescence is emitted by the radiative recombination of these electrons with holes trapped at the copper acceptor level.

The mechanism of the killer effect of iron group ions was discussed by some investigators about twenty years ago.⁵⁻⁷⁾ It was considered that iron group ions create some deep levels in the forbidden gap, and the killer effect is caused by the bypassing process. In this process, a part of conduction electrons are captured by the deep levels due to iron group ions, and are made to recombine with holes in the valence band nonradiatively, as schematically shown in Fig. 1(d). However, one will easily point out another possibility that a part of excitation energy is transferred nonradiatively from the luminescence centers to iron group ions as shown in Fig. 1(c), and consequently the visible luminescence is quenched.⁸⁾ Iron group ions have many 3d energy levels split by crystal field. The excitation energy transferred to iron group ions is relaxed through these levels and finally annihilated by the emission of a photon with a small energy or of some phonons.

§2. Samples

The samples used were ZnS: Cu, Al powder phosphors doped with iron group ions M^{2+} ($M^{2+} = Mn^{2+}$, Fe^{2+} , Ni^{2+} , and Co^{2+}), as well as ZnS single crystals doped with M^{2+} ions. The powder phosphors were prepared by the ordinary method. The firing was made in H_2S atmosphere at $1150^\circ C$. Copper acceptor, aluminum donor, and M^{2+} ions were added as the form of aqueous solutions of sulfate salts. The amounts of copper and aluminum were 4×10^{-4} and 8×10^{-4} mole/mole ZnS, respectively. The amounts of M^{2+} ions added in the preparation procedure were changed in wide ranges, namely in a range of 10^{-7} – 10^{-4} mole/mole ZnS for Fe^{2+} , Ni^{2+} , and Co^{2+} , and of 10^{-4} – 3×10^{-2} for Mn^{2+} . The amounts of these ions contained in the phosphors were determined by chemical analysis. These samples of powder phosphors were used for the measurements of luminescence properties and their dependences on M^{2+} ions doped.

ZnS single crystals doped with M^{2+} ions were

grown from the melt under high argon pressure by the Bridgman method. The detail of the procedure has been described in a previous paper.⁹⁾ The starting materials for the crystal growth were ZnS powders containing M^{2+} ions, which were prepared by the firing in H_2S atmosphere at $1150^\circ C$. The amounts of iron group ions doped were 5×10^{-4} – 10^{-2} mole/mole ZnS. These single crystal samples were used for the measurements of absorption spectra due to M^{2+} ions and also of photoconductivity.

The valency of the iron group ions doped is considered to be surely divalent from the following reasons. The powder samples were prepared by the firing in H_2S atmosphere which has reducing nature. The atmosphere of the crystal growth under high argon pressure is considered to be neutral or rather reducing, since both the crucible and heater are made of graphite. Furthermore, the absorption spectra of these ions in single crystals are well interpreted by the crystal field theory assuming the divalent state.

§3. Experimental Results and Discussion

The dependences of the intensity of the G-Cu luminescence in ZnS: Cu, Al(M) powder phosphors on the concentrations of M^{2+} ions were measured under the 365 nm light excitation from a mercury lamp at room temperature and 4.2 K. The results are shown in Fig. 2. It is observed that the strength of the killer effect is an order of $Ni^{2+} > Fe^{2+} \geq Co^{2+} > Mn^{2+}$, and that the effect is more pronounced at room temperature than at 4.2 K, except the case of Fe^{2+} in which for concentrations more than 8×10^{-5} mole the effect is a little stronger at 4.2 K.

To study the effect of M^{2+} ions on the decay characteristics, time-resolved emission spectra were measured in a region of 10–1500 μs . A xenon flash lamp producing light pulses of 2 μs duration was used, and the light with wavelengths around 360 nm was selected for excitation. The detail of the method has been described in a previous paper.²⁾ The decay characteristics of the G-Cu luminescence is approximated, except very early stage, by the following equation, reflecting the features of donor-acceptor pair emission,¹⁰⁾ as was found in a previous paper.²⁾

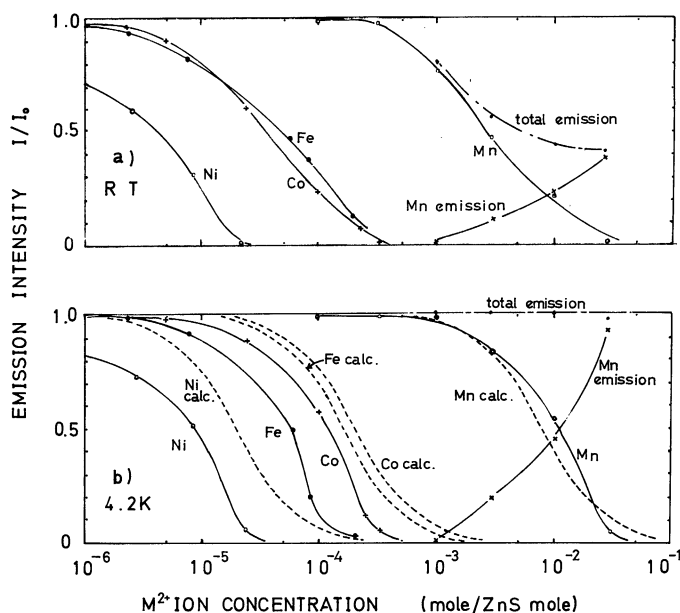


Fig. 2. Solid curves are the dependences of the intensity of the G-Cu luminescence in ZnS: Cu, Al(M) on the concentrations of M^{2+} ions (Mn^{2+} , Fe^{2+} , Ni^{2+} , and Co^{2+}) at (a) room temperature and (b) 4.2 K. In the case of Mn^{2+} ion, the intensity of the Mn^{2+} orange luminescence and the total of the intensities of the G-Cu and Mn^{2+} luminescences are also shown. Dotted curves in (b) are calculated ones assuming the killer effect due to resonance energy transfer (see the text).

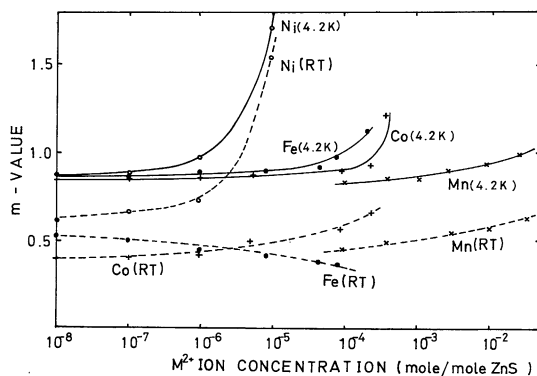


Fig. 3. Dependences of the m -value in the decay characteristics of the G-Cu luminescence in ZnS: Cu, Al(M) on the concentrations of M^{2+} ions (Mn^{2+} , Fe^{2+} , Ni^{2+} , and Co^{2+}) at room temperature and 4.2 K.

$$I \propto t^{-m}, \quad (1)$$

where m has values around unity depending on excitation intensity.

Figure 3 shows the dependence of the m -value on the concentration of M^{2+} ions at room temperature and 4.2 K. It is observed that the m -value increases, in other words, the decay rate of the G-Cu luminescence becomes faster

with increasing the concentration of M^{2+} ions at both temperatures, except the case of Fe^{2+} at room temperature in which the m -value decreases contrary to the other cases. The increase of the m -value indicates that the killer effect of M^{2+} ions is operative even during the decay of the G-Cu luminescence. The results of the figure indicate that the strength of the killer effect during decay at 4.2 K is an order of $Ni^{2+} > Fe^{2+} \geq Co^{2+} > Mn^{2+}$.

In this measurement the samples were immersed in liquid helium in an optical cryostat. At 4.2 K one can completely neglect the thermal ionization process of electrons from the aluminum level and also that of holes from the copper level during decay of luminescence. Therefore, the killer effect due to the bypassing process via the levels of M^{2+} ions does not take place after the cessation of excitation at 4.2 K. The observed fact that the m -value increases with increasing the M^{2+} ion concentration is regarded as clearly indicating that the killer effect due to nonradiative energy transfer from the G-Cu luminescence centers to M^{2+} ions takes place during decay at 4.2 K. If there are some overlaps between the G-Cu

emission spectrum and the absorption spectra of M^{2+} ions, excitation energy will be resonantly transferred to M^{2+} ions, and then it will be dissipated by the emission of long wavelength light or of phonons.

In order to see the aspect of these spectral overlap, the absorption spectra of ZnS: M single crystals were measured at 4.2 K by using a Carry Model 14 spectrophotometer. In this measurement, an undoped ZnS crystal was used as the reference to cancel the absorption of the ZnS host, and the spectra of the absorption cross-sections of M^{2+} ions were obtained. The results are shown in Fig. 4, together with the G-Cu emission spectrum. It is observed that there are spectral overlaps for all M^{2+} ions.

The theory of resonant energy transfer from an energy donor to an acceptor is well established.¹¹⁾ The problem in the present case is what type of interaction is responsible for the energy transfer. The G-Cu luminescence is due to the recombination of electrons trapped at aluminum donors with holes trapped at copper acceptors, and is surely caused by a dipole-transition. Most part of the absorption spectra

of M^{2+} ions in Fig. 4 are due to d-d transitions within these ions, which are forbidden in free ion state. It was shown^{12,13)} that in the ZnS host these transitions are made dipole-allowed by the tetrahedral crystal field which has no inversion symmetry. Therefore, we tentatively assume that dipole-dipole interaction dominates the energy transfer from the G-Cu luminescence centers to M^{2+} ions, and attempt to calculate the dependences of the G-Cu luminescence intensity on the M^{2+} concentrations caused by the energy transfer.

The probability of resonance energy transfer from an energy donor to an acceptor due to dipole-dipole interaction is given by¹¹⁾

$$P_{DA}(dd) = \frac{3\hbar^4 c^4}{4\pi n^4 R^6 \tau_D} \int \frac{F_D(E) f_A(E)}{E^4} dE, \quad (2)$$

where $F_D(E)$ is the normalized emission spectrum of the donor, $f_A(E)$ is the absorption spectrum of the acceptor expressed by unit of absorption cross-section, R is the distance between the donor and acceptor, τ_D is the decay time of the donor emission in the absence of acceptors, and n is the refractive index of the host. The spectral overlap integral, $\int [F_D(E) \times f_A(E)/E^4] dE$ was estimated for each M^{2+} ion in an energy region of 2.2–3.0 eV from Fig. 4. The results are shown in Table I.

The magnitudes of the overlap integrals are in an order of $Ni^{2+} > Fe^{2+} \geq Co^{2+} > Mn^{2+}$, and the ratio is $1: 1.3 \times 10^{-2}: 1.1 \times 10^{-2}: 1.2 \times 10^{-5}$. This order is in agreement with that of the strength of the killer effect during decay at 4.2 K obtained by the dependence of the m -value on the M^{2+} ion concentration as shown in Fig. 3. This is a quite reasonable fact. Further this order accords with that of the killer effect as observed as the concentration dependence of the luminescence intensity under steady excitation at 4.2 K as shown in Fig. 2(b). This implies that the nonradiative energy

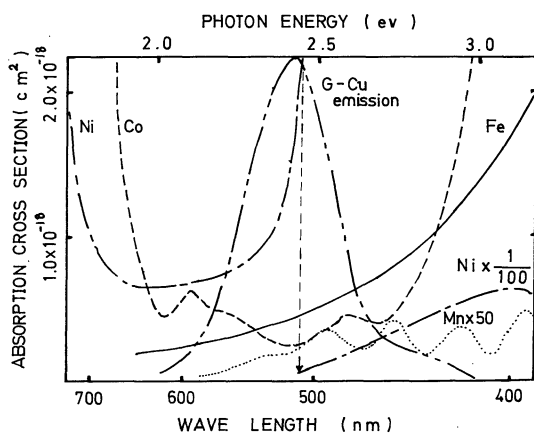


Fig. 4. Absorption spectra of ZnS: M single crystals ($M^{2+} = Mn^{2+}, Fe^{2+}, Ni^{2+}$, and Co^{2+}) and the G-Cu emission spectrum at 4.2 K.

Table I. Spectral overlap integral, critical transfer distance R_0 , and critical transfer concentration C_0 for ZnS: Cu, Al(M) ($M^{2+} = Mn^{2+}, Fe^{2+}, Ni^{2+}$, and Co^{2+}).

	$\int \frac{F_D(E) f_A(E) dE}{E^4} (cm^2)$	$R_0 (\text{\AA})$	$C_0 (\text{mole/ZnS mole})$
Ni^{2+}	1.02×10^{-16}	38.5	7.12×10^{-5}
Fe^{2+}	1.38×10^{-18}	18.8	6.24×10^{-4}
Co^{2+}	1.17×10^{-18}	18.3	7.79×10^{-4}
Mn^{2+}	1.22×10^{-21}	5.82	2.41×10^{-2}

transfer is an important cause for the killer effect under steady excitation.

The dependence of donor luminescence intensity under steady excitation I on acceptor concentration C due to energy transfer of dipole-dipole interaction was given theoretically by Eisenthal and Siegel¹⁴⁾ as follows.

$$I/I_0 = 1 - \frac{\pi C}{2C_0} \exp\left(\frac{\sqrt{\pi}C}{2C_0}\right)^2 \left[1 - \operatorname{erf}\left(\frac{\sqrt{\pi}C}{2C_0}\right)\right],$$

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-\xi^2) d\xi, \quad (3)$$

where I_0 is the donor luminescence intensity in the absence of acceptors, and C_0 is the critical transfer concentration of acceptor defined from the critical transfer distance R_0 as $C_0 = 3/4\pi R_0^3$. R_0 is the distance of a donor-acceptor pair at which the probability of energy transfer becomes equal to that of the radiative transition of the donor. One can calculate R_0 for each M^{2+} ion from eq. (2) by putting that $P_{DA}(dd) = 1/\tau_D$. The results are shown in Table I. Using these values of R_0 , eq. (3) has been plotted in Fig. 2(b) by dotted lines for each M^{2+} ion.

It is observed in Fig. 2(b) that in the cases of Ni^{2+} , Fe^{2+} , and Co^{2+} ions the experimental curves are considerably shifted to the low concentration side from the calculated curves. This implies that the observed killer effect of these three ions can not be interpreted only by the assumption that the nonradiative energy transfer is responsible for the effect. In the case of Mn^{2+} ion, on the other hand, the experimental curve seems roughly in agreement with the calculated one. However, it is noticed that there is the tendency that the experimental curve is a little above the calculated one in the intermediate concentration range, and is a little below it in the high concentration range. This might imply that the interaction responsible for the energy transfer is not dipole-dipole one, but is some shorter-range interaction than dipole-dipole interaction such as dipole-quadrupole interaction. The total of the intensities of the G-Cu luminescence and Mn^{2+} orange luminescence is constant at 4.2 K as shown in the figure. One may conclude that the killer effect of Mn^{2+} ion at 4.2 K is caused mostly by the nonradiative resonance energy transfer, although the interaction responsible might not be dipole-dipole one.

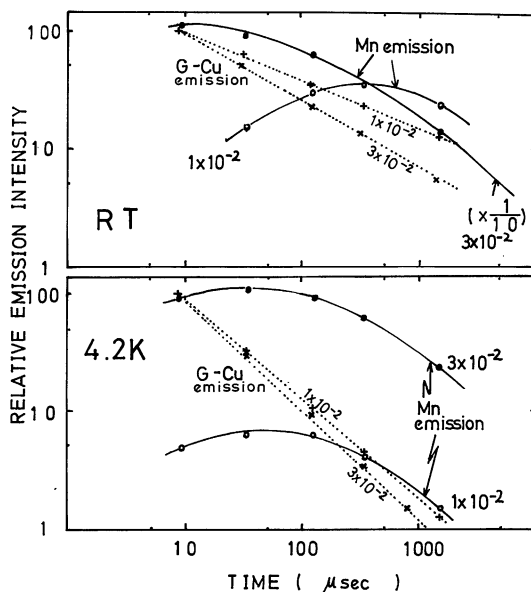


Fig. 5. Time change of the intensities of the G-Cu and Mn^{2+} luminescences after the pulse excitation in ZnS: Cu, Al(Mn^{2+}) ($Mn^{2+} = 1$ and 3×10^{-2} mole/mole ZnS) at room temperature and 4.2 K.

The observation of the transient behavior of the G-Cu and Mn^{2+} luminescences presents further evidence that nonradiative energy transfer takes place from the G-Cu centers to the Mn^{2+} centers. Figure 5 shows the time change of the intensities of the G-Cu and Mn^{2+} luminescences after pulse excitation. It is seen that at both 4.2 K and room temperature the Mn^{2+} luminescence rises after pulse excitation and then decays. The time constant of the rise is 40–50 μs at 4.2 K. This time constant represents that for the energy transfer from the G-Cu to Mn^{2+} centers.

In the cases of Ni^{2+} , Fe^{2+} , and Co^{2+} ions there is considerable disagreement between the experimental and calculated curves for the I/I_0 vs. C relation as shown in Fig. 2(b). This fact leads one to consider that some mechanism is operating for the killer effect of these ions in addition to the mechanism of nonradiative energy transfer. As mentioned in §1, it was considered, in the discussion on the killer effect made previously, that this effect is caused by the bypassing process via deep levels of M^{2+} ions. It is well known that in ZnS phosphors involving small amounts of killer ions a superlinear relation of luminescence intensity vs. excitation intensity is observed. This fact was interpreted by the bypassing process.^{5,6)} At lower excitation

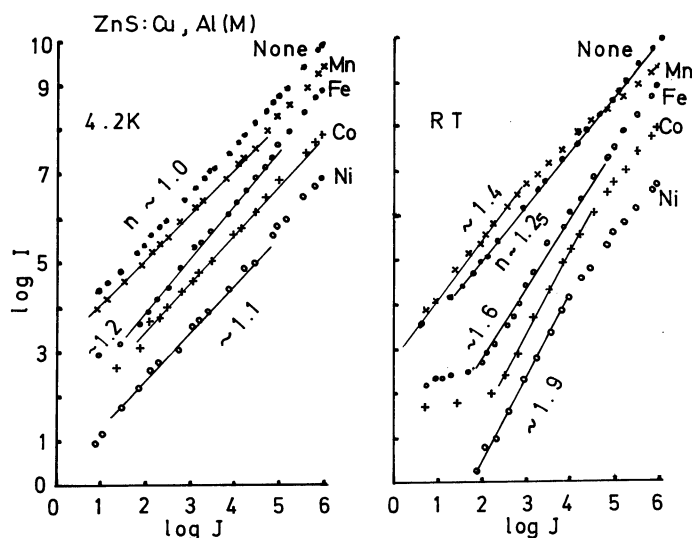


Fig. 6. Relations of the G-Cu luminescence intensity I vs. excitation intensity J for ZnS: Cu, Al(M) (M=none, Mn^{2+} , Fe^{2+} , Ni^{2+} , and Co^{2+}) at room temperature and 4.2 K.

intensities the number of excited centers is much smaller than that of killer centers, so that most of excited electrons and holes recombine via killer centers and the luminescence has low efficiencies. On the other hands, at higher excitation intensities the number of excited centers becomes much larger than that of killer centers, so that the killer effect relatively little works, giving rise to high efficiencies. In the intermediate region, therefore, the superlinear luminescence appears. The analysis based on this interpretation was developed by Roberts and Williams,⁷⁾ and further by Duboc¹⁵⁾ and by Klasens.¹⁶⁾

In order to examine whether the bypassing process is important in the present case, the relation of the G-Cu luminescence intensity I vs. excitation intensity J was measured at both 4.2 K and room temperature changing the range of J over five orders of magnitude. The 365 nm light was used for excitation. The maximum excitation intensity corresponds to 3×10^{16} photons $\cdot \text{cm}^{-2} \text{s}^{-1}$. The results are shown in Fig. 6.

At 4.2 K, the slope n of the I vs. J relation is nearly unity in the cases of none (no M^{2+} ions doped) and Mn^{2+} ion, while in the cases of Fe^{2+} , Ni^{2+} , and Co^{2+} ions the slope is a little more than unity. At room temperature, on the other hand, the slope is fairly larger than unity in all the cases. Considerable superlinear relations are observed in the cases of Fe^{2+} , Co^{2+} ,

and Ni^{2+} ions. Even in the case of none, a superlinear relation is observed. One may attribute this fact to the presence of very small amounts of iron group ions or some other impurities inevitably involved. The slope of Mn^{2+} ion is a little larger than that of none. It is sure that the superlinear relations are enhanced at room temperature in comparison with 4.2 K.

The bypassing process responsible for the superlinear relations is considered to be caused by the capture of conduction electrons by the deep levels created by doped M^{2+} ions. To examine this, photoconductivities of ZnS: M^{2+} single crystals were measured at 4.2 K and room temperature under the irradiation of the 313 nm light from a mercury lamp. This light corresponds to the band-to-band excitation in the ZnS host. The concentration of M^{2+} ions was 10^{-3} mole/mole ZnS for all the ions. It was found that the doping of M^{2+} ions quenches photoconductivity, and the quenching in the cases of Fe^{2+} , Ni^{2+} , and Co^{2+} ions is very remarkable. The ratio of the magnitude of photocurrent was none: Mn^{2+} : Fe^{2+} : Ni^{2+} : Co^{2+} = 1: 0.93: 6.9×10^{-5} : 6.2×10^{-6} : 4.6×10^{-6} at 4.2 K and 1: 0.71: 8.1×10^{-5} : 3.8×10^{-6} : 4.1×10^{-6} at room temperature, respectively. The quenching of photoconductivity will be ascribed to the decrease of the lifetime of conduction electrons. One may regard the observed facts as presenting evidence that M^{2+}

ions create deep trapping levels so that they cause the superlinear luminescence due to the bypassing process.

As mentioned above, it was observed that the superlinear luminescence is enhanced with increasing temperature. Also in Fig. 2, it is seen that the killer effect is generally more pronounced at room temperature than at 4.2 K. These facts are interpreted in the following way. The killer effect due to the bypassing process is dominated by the competition of the capture of an electron by the aluminum donor level and the deep level due to M^{2+} ions. In the equilibrium state as under steady excitation, the rate of the capture of an electron is balanced with that of the thermal release.¹⁷⁾ Then, one sees that the rate of the capture by a trap with a depth E is proportional to $\exp(-E/kT)$. The thermal depth of the aluminum level was estimated to be 0.074 eV.⁹⁾ The depths of the levels due to M^{2+} ions are assumed to be larger than the aluminum depth. Then the ratio of the rate of the capture by the aluminum level to that by the M^{2+} level, R_{Al}/R_M , should increase with temperature, and R_{Al}/R_M (4.2 K) $\gg R_{Al}/R_M$ (room temperature). Therefore, the killer effect due to the bypassing process should be much more pronounced at room temperature than at 4.2 K.

Fe^{2+} ion shows some unusual behaviors; namely, in Fig. 2 the killer effect is a little weaker at room temperature than at 4.2 K for concentrations more than 8×10^{-5} mole, and further in Fig. 3 the m -value decreases with increasing the concentration at room temperature contrary to the cases of other M^{2+} ions. These unusual behaviors of Fe^{2+} ion are not understood for the moment.

Let us discuss the case of Mn^{2+} ion more in detail. As seen in Fig. 2, the total of the intensities of the G-Cu and Mn^{2+} orange luminescences is kept constant with increasing the Mn^{2+} concentration at 4.2 K, but it is rapidly decreased at room temperature. To examine the cause for this fact, the temperature dependences of the intensities of the G-Cu and Mn^{2+} luminescences were measured in the region from 77 to 300 K under the irradiation of the 365 nm light. It was observed that the intensity of the G-Cu luminescence in the phosphor without Mn^{2+} ions is almost temperature-independent. However, in the phosphors

containing Mn^{2+} ions both the intensities of the G-Cu and Mn^{2+} luminescences decrease in a similar manner with increasing temperature above about 200 K. Further this tendency of the temperature quenching is enhanced with increasing the Mn^{2+} concentration.

It is expected from eq. (2) that the probability of resonant energy transfer from the G-Cu luminescence center to the Mn^{2+} center is almost temperature-independent, since the spectral overlap integral shown in Fig. 4 little changes with temperature. If one attempts to adjust the observed data for the G-Cu and Mn^{2+} luminescences at room temperature in Fig. 2, so that the total of the intensities of these luminescences become unity independently of the Mn^{2+} concentration, one finds that the curves of these two luminescences change to those which are nearly the same as observed at 4.2 K. This treatment is considered to indicate that the excitation energy resonantly transferred from the G-Cu center to the Mn^{2+} center is converted to the Mn^{2+} luminescence with the probability independent of the Mn^{2+} concentration, in other words, the nonradiative dissipation of the energy within the Mn^{2+} center hardly takes place. Then, in order to understand the decrease of the total of the intensities of the G-Cu and Mn^{2+} luminescences with increasing the Mn^{2+} concentration and also the temperature quenching of the G-Cu luminescence enhanced by Mn^{2+} ion, one must assume that Mn^{2+} ion also exerts the killer effect due to the bypassing process, which is neglected at 4.2 K but becomes appreciable with increasing temperature. This assumption is supported by the fact that the slope of the I vs. J relation for Mn^{2+} ion is a little larger than that of none at room temperature as shown in Fig. 6.

§4. Concluding Summary

The mechanism of the killer effect of iron group ions ($M^{2+} = Mn^{2+}$, Fe^{2+} , Ni^{2+} , and Co^{2+}) on the green luminescence in ZnS: Cu, Al phosphors is investigated. The killer effect has been considered to be caused by the bypassing process via deep levels created by M^{2+} ions. However, another possibility is pointed out that the killer effect is due to nonradiative resonance energy transfer from the G-Cu centers to the M^{2+} centers.

The decay rate of the G-Cu luminescence is

found to become faster with increasing the concentrations of M^{2+} ions at 4.2 K. This fact clearly indicates that the killer effect due to resonance energy transfer takes place during decay at 4.2 K. Assuming dipole-dipole interaction to be responsible for the energy transfer, the dependence of the G-Cu luminescence intensity on the concentrations of M^{2+} ions is theoretically calculated by the use of the spectral overlap integrals experimentally obtained. As a result of the comparison with experiment, it is concluded that the killer effect of Mn^{2+} ion at 4.2 K is caused mostly by the resonance energy transfer. In the case of Fe^{2+} , Ni^{2+} , and Co^{2+} ions the observed killer effect is stronger than expected from the above-mentioned calculation. In order to examine whether the killer effect due to the bypassing process takes place, the relation of the G-Cu luminescence intensity vs. excitation intensity and also photoconductivity are measured. It is found that Fe^{2+} , Ni^{2+} , and Co^{2+} ions bring about remarkable superlinear relations and the quenching of photoconductivity. It is concluded that the killer effect of these ions is caused not only by the resonance energy transfer but also by the bypassing process, and that the effect due to the bypassing process is enhanced with increasing temperature. The behavior of Mn^{2+} ion at room temperature is not well understood only by taking account of the resonance energy transfer.

One must assume that Mn^{2+} ion also exerts the killer effect due to the bypassing process, which is neglected at 4.2 K but becomes appreciable with increasing temperature.

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