only the first two compounds were found to have pyrochlore-type structures. The other four compounds show complicated powder patterns, and no effort was made further to interpret them. $Pb_2Ta_2O_7$ shows, as does $Pb_2Nb_2O_7$, a rhombohedral lattice; and $Y_2Ti_2O_7$ shows a cubic lattice. No dielectric anomaly was found for $Pb_2Ta_2O_7$ or $Y_2Ti_2O_7$ between 20°C and −180°C. The dielectric constants of these pyrochlore types are relatively high in general, which fact renders them worth examining. Hulm[4] reported no anomaly in $Cd_2Ta_2O_7$, $Pb_2Ta_2O_7$, $In_2Ti_2O_7$, or $In_2Zr_2O_7$. The structure of the last two compounds is unknown.

To date, no rules are known according to which one can judge whether or not a compound of constitution $A_2B_2O_7$ is likely to have a pyrochlore structure. However, the following may be said upon consideration of the ionic radii of the involved ions. It does seem that a pyrochlore structure can be realized for only a narrow range of ionic radii: 0.95 to 1.15 A for ion A and 0.60 to 0.70 A for ion B. (It should of course be possible to include small amounts of other ions in the network, thus accounting for the large number of mineral varieties in this species.) $Cd_2Nb_2O_7$ has the smallest A ion and the largest B ion in this range, and this might be related to the fact that the Curie temperature of $Cd_2Nb_2O_7$ is always shifted downward upon replacement of Cd or Nb by other ions. This critical condition on ion size is in contrast with the case of the perovskite-type structure of composition ABO_3. A large number of crystals have been reported as members of this group, with a relatively wide range of ionic radii for A and B; and several of the members have been found to be ferroelectric. A good number of other types of multiple oxides containing Nb, Ta, and/or Ti deserve examination, and some of them are under study in our laboratory.

ACKNOWLEDGMENTS

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Model for Luminescence and Photoconductivity in the Sulfides

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A model for sulfides activated by monovalent metals is discussed which differs in several important respects from that usually employed. Because of the net negative charge of the lattice volume surrounding the activator there is a large cross section for trapping of holes which may be accompanied by release of a large amount of energy. This is presumed to be the transition leading to luminescence. A subsequent trapping of an electron returns the center to its original condition. For the electron trapping there is no Coulomb field and both the capture cross section and energy released would be expected to be small compared with the case of hole trapping. On the basis of this model, there is a simple explanation of the fast luminescence decay associated with hole capture and the slow conductivity decay associated with that of free electrons. Other well-known phenomena in the sulfides are examined on the basis of this model. In addition, predictions of this model concerning the infrared photoconductivity and infrared stimulation of luminescence have been verified by experiment on silver-activated cadmium sulfide.

I. INTRODUCTION

THERE exists an extensive literature on both the luminescence and conductivity properties of the sulfide phosphors. Impurity-activated sulfides have been among the earliest materials studied, and in recent years have been the subjects of intensive investigations, stimulated in part by their many practical applications. A recent paper by Klasens[1] summarizes much of the current theory of luminescence for sulfides. Similarly a large amount of work has been done on the conductivity of sulfides, particularly on cadmium sulfide which can be prepared in the form of fairly large crystals by the method of Frerichs,[2] and which is of special practical interest because of its unusually high photosensitivity. An introduction to the literature on the conductivity of cadmium sulfide may be found in a paper by Rose.[3] Schön[4] and Klasens and his associates[5] have proposed a "hole migration" theory of luminescence of sulfides activated with monovalent impurities such as Ag^+. This theory is illustrated in Fig. 1 for the case where excitation of luminescence is by absorption of light in the fundamental band of the host lattice. The sequence of events is as follows:

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[1] H. A. Klasens, J. Electrochem. Soc. **100**, 72 (1953).

[2] R. Frerichs, Naturwiss. **33**, 381 (1946).

[3] A. Rose, RCA Rev. **12**, 362 (1951).

[4] M. Schön, Z. Physik **119**, 463 (1942).

[5] H. A. Klasens, Nature **158**, 306 (1946); Klasens, Ramsen, and Quantie, J. Opt. Soc. Am. **38**, 60 (1948).

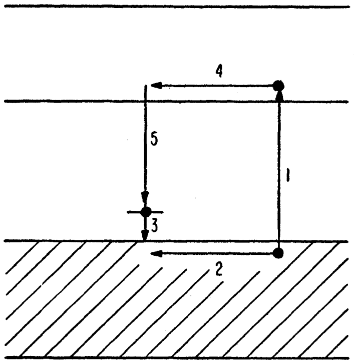

FIG. 1. Conventional model for sulfides with monovalent activator (1) excitation; (2) hole migration; (3) hole capture (nonradiative); (4) electron migration; (5) electron capture resulting in luminescence.

(1) Light is absorbed in the fundamental absorption band producing a free electron and hole and leading to photoconductivity.

(2) The hole may migrate toward the impurity center. If, for example, the center is due to Ag^+ substituted for Cd^{++} in CdS, then the center has a net negative charge and attracts the hole with a Coulomb-like attraction.

(3) The hole is captured by the impurity center, giving off a small amount of energy as infrared radiation or as vibrational quanta.

(4) The electron wanders through the lattice until it finally comes near the center.

(5) The electron is captured by the center. It recombines with the captured hole and gives off energy as luminescent emission. The electronic transition may be directly from the conduction band to the ground state of the center, or may be by way of an intermediate excited state of the center. After luminescence the cycle is complete and the process may again be repeated.

By extending this model to include two impurity atoms, Schön and Klasens are able to account for the effect of poisons, variations of luminescence color with temperature of some phosphors, the nonlinear relationship between luminescent output and the exciting intensity, and other similar phenomena in the sulfides.

Another important development in the theory of the sulfides has been the work of Kröger and his associates,[6] who showed that in zinc sulfide it is necessary to balance each monovalent positive ion introduced by a monovalent negative ion or a trivalent positive ion. This "charge compensation" principle serves to explain the role of fluxes normally used to prepare these phosphors. In addition it emphasizes the essentially ionic nature of the impurity center. Thus even if the sulfide lattice is primarily covalent in character, it appears that in the vicinity of most impurities the ionic character of the impurity is decisive. Recently Klasens[1] has suggested that the luminescent center is actually a sulfide ion perturbed by the presence of the activator ion, rather than the activator ion itself. This modification of the theory does not essentially alter the sequence of events previously described in the luminescent process.

While a major part of the work on sulfides has dealt either with the luminescence or conduction properties separately, some investigations have been made on both properties simultaneously. One very striking fact which emerges from such investigations is that the decay of luminescence is much more rapid than the decay of photoconductivity. On the basis of the model of Fig. 1, it would be expected that the decay times of luminescence and photoconductivity would be approximately alike since the capture of the electron in step 5 leads to both luminescence and to a decrease in conductivity. Several attempts have been made to explain this phenomenon. Bube[7] has suggested that in ZnS the luminescence might be typical of the crystal and that the conductivity is characteristic of a small surface layer. Kallman and Kramer[8] postulate that electron transfer occurs in the crystal in some cases without having electrons enter the conduction band. McKay[9] has investigated the conductivity of *n-p-n* junctions and inferred that the slow current decay may be characteristic of such junctions. Each of these suggestions involves the assumption that the crystal has regions in which the properties are different from those of the bulk of the crystal.

The band picture of Fig. 1 is oversimplified in that a variety of other levels may enter and be of importance. One set of levels is due to the "quenching" centers which have been investigated by Hardy[10] and Taft and Hebb.[11] If a small current is drawn from the crystal by applying an electric field and irradiating in the fundamental absorption band, additional irradiation in the quenching bands first causes a transient increase and then a steady decrease in current flow. For CdS, the edge of the fundamental absorption band is at about 5000 A and the quenching bands are about 10 000 A. Rose[3] and Taft and Hebb[11] interpret absorption in these centers as excitation of a hole from an acceptor level to the valence band. The free holes which are produced in this process first add to the number of charge carriers and the conductivity is increased. In the steady state condition, however, these holes recombine with electrons resulting in a decreased concentration in the conduction band and, since Hall effect measurements indicate that electrons are the principal charge carriers, the conductivity is observed to decrease.

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[6] F. A. Kröger and J. F. Hellingman, J. Electrochem. Soc. **93**, 156 (1948); **95**, 68 (1949); F. A. Kröger and J. Dikhoff, Physica **16**, 297 (1950).

[7] R. H. Bube, Phys. Rev. **83**, 393 (1951).

[8] H. Kallman and B. Kramer, Phys. Rev. **87**, 91 (1951).

[9] K. G. McKay, Phys. Rev. **84**, 833 (1951).

[10] A. E. Hardy, J. Electrochem. Soc. **87**, 355 (1945).

[11] E. A. Taft and M. H. Hebb, J. Opt. Soc. Am. **42**, 249 (1952).

Another set of fairly deep electron traps is introduced by the charge compensation centers when a monovalent metal substitutes for a divalent positive ion of the host lattice. There is evidence that these centers can consist of trivalent positive ions substituted at divalent positive ion sites, monovalent negative ions substituted at divalent negative ion sites, or negative ion vacancies. In each case a deep electron trap should be formed involving a Coulomb attraction for the electron.

In addition to these centers, there appear to be a variety of traps of varying depths which are less well understood but which may, in practice, determine some of the properties of materials used experimentally.

II. PROPOSED MODEL

In this section a somewhat different model is proposed. The model is illustrated in Fig. 2 and differs from Schön's and Klasen's model in that the trapping of the hole by the center is considered to be a large energy transition and is assumed to give rise to luminescence. On an ionic picture of the center, the substitution of a monovalent positive ion for a divalent one leaves the volume around the center with a net negative charge. This has two effects: first, the cross section for trapping of a hole becomes large because of the Coulomb attraction; and second, the energy released in the capture of a hole may be large. The proposed cycle is then as follows:

(1) Light is absorbed producing a free hole and electron leading to conductivity.

(2) The hole and electron move in their respective bands, and eventually the hole migrates near the impurity center.

(3) The hole is captured by the impurity center and luminescent emission occurs leaving the center now neutral in charge.

(4) The electron wanders through the lattice until it finally comes near the center.

(5) The electron is finally captured by the center, and in the capture only a small amount of energy is given off as infrared radiation or as vibrational quanta. The center is now returned to its initial condition and the cycle can be repeated.

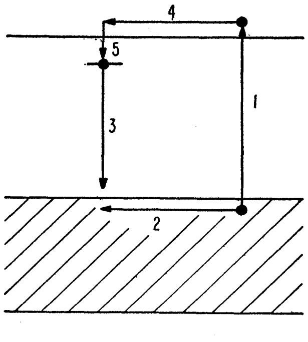

FIG. 2. Proposed model for sulfides with monovalent activator: (1) excitation; (2) hole migration; (3) hole capture resulting in luminescence; (4) electron migration; (5) electron capture (nonradiative).

The essential difference between the conventional model and the model presented here is that the former assumes that luminescence results from the capture and subsequent recombination of a conduction electron, whereas the latter assumes that luminescence results from the capture and subsequent recombination of a free hole. As has been assumed by Klasens,[1] the levels involved here arise from sulfur ions adjacent to the monovalent activator. On the basis of the model proposed here, however, it is assumed that the energy required to free an electron from one of these sulfur ions is small. There is a long-wavelength extension of the fundamental absorption band which arises when monovalent activator ions are introduced into sulfides. This would be interpreted as arising not from sulfur ions immediately adjacent to the monovalent activator, but from sulfur ions further removed. These levels would be shifted slightly above the valence band due to the negatively charged luminescent center.

The luminescence of "self-activated" sulfides may be considered as similar to that due to monovalent metals both on Klasen's model and that proposed here if the center is that proposed by Kröger and Vink[12]: a positive-ion vacancy whose nearest surroundings have lost one electron.

The difficulty of choosing a model for sulfides on the basis of a limited variety of experiments is emphasized by Duboc[13] who has shown that the nonlinearity of luminescence and photoconductivity with exciting intensity in photoconducting phosphors can be explained with at least sixteen different two-center models. It appears, therefore, that only by examining a variety of experimental data is it possible to reach conclusions concerning the correctness of a model.

III. COMPARISON WITH EXPERIMENT

An attempt will be made to relate the model proposed here to various phenomena in sulfides. In addition, several experiments have been performed involving luminescence and photoconducting properties of sulfides at low temperatures under infrared excitation in order to check the predictions of this model.

Mention has already been made of the fact that, typically, the decay time of photoconductivity is two orders of magnitude larger than the decay time of luminescence. While the explanations which have been advanced involve the assumption that there are special regions of the crystal with properties different from the main crystal, it is also possible to invent a scheme, based on the Schön-Klasens model (Fig. 1), to explain this effect. We may postulate that killer centers exist in addition to luminescent centers. The killer centers should have the property that recombination of

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

[13] C. A. Duboc, Brit. J. Appl. Phys. **107**, Suppl. No. 4 (1955).

electrons and holes at the center does not result in visible luminescence. Also the centers should have levels high enough above the top of the filled band so that thermal release of trapped holes does not occur to an appreciable extent at ordinary temperatures. Finally, the killer center should have a large cross section for trapping of holes but only a small cross section for trapping of an electron once the hole has been captured. On illumination in the fundamental absorption band, then, free electrons and holes are released and the holes are first trapped at killer centers until these are filled leaving a number of free electrons in the conduction band. As excitation proceeds, holes are trapped at the luminescent centers and electrons quickly combine with these holes to give off luminescence. When the exciting light is removed the luminescent process quickly ceases, but because of the low cross section for capture of electrons by the killer centers, the electrons which will recombine with holes at these centers remain in the conduction band for a long time. In this way long-decay photoconductivity and short-decay luminescence could occur without seriously impairing the high luminescence efficiency under steady excitation.

The same results are obtained from the model proposed in this paper without using centers other than the luminescent centers. In Fig. 2 the hole-trapping process of step 3 is one for which there is presumed to be a large cross section due to Coulomb attraction, and this leads to luminescence. The subsequent trapping of an electron in step 5 may have a very small cross section and lead to the slow photoconductive response.

The change of luminescent color with temperature of doubly activated phosphors has been adequately explained on the Schön-Klasens model. On the basis of the model proposed here, this phenomena would be interpreted as follows. We suppose the electron in one center lies closer to the conduction band than the electron in the other center (Fig. 3). As the phosphor is warmed up from low temperatures, the electron in the shallower center will be thermally ejected into the conduction band and the center will become inactive as far as luminescence is concerned. The observed luminescence would then tend to become more and more characteristic of the deeper-lying center. Such behavior could thus give rise to the well-known blue to green color shift of ZnS:Ag,Cu for example.

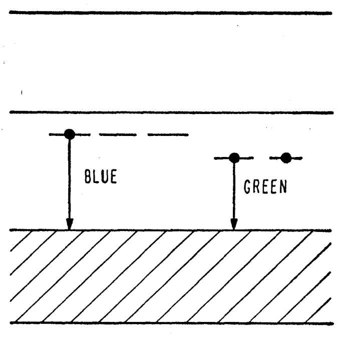

FIG. 3. Explanation of color change in luminescence on the basis of proposed model. The blue levels are thermally emptied as the temperature is raised.

It is evident that on the basis of the above qualitative arguments, both the conventional model and the model proposed here are capable of explaining many of the observed properties of photoconducting phosphors. Although the proposed model does seem to afford a simpler interpetation of luminescent and photoconductive decay times, there is in the above discussion no overriding evidence favoring one or the other. Therefore, in order to clarify some of the issues raised here, an experimental investigation of silver-activated CdS crystals was undertaken on the properties of these phosphors under infrared excitation.

When measured at 77°K, silver-activated CdS shows a broad emission band centering at about 6100 A.[14] A study of the decay times of this luminescence and the associated photoconductivity at 77°K shows that the decay time of the luminescence is about one-hundredth the decay time of the photoconductivity.[15] A number of experiments in the infrared region were performed on this phosphor to discover whether silver activation introduced an electronic level lying just below the conduction band as suggested by the new model. The crystals used in this work were activated with silver by introducing silver vapor into the vapor phase growth of CdS.

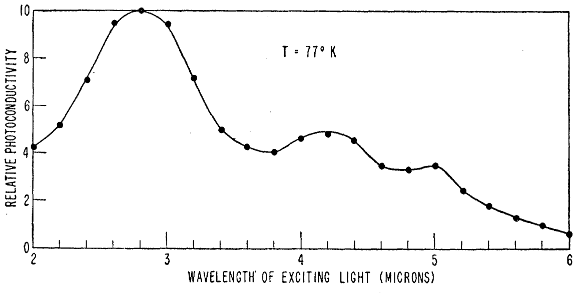

FIG. 4. Infrared photoconductive response of CdS(Ag) at 77°K for equal number of incident quanta.

Most of the experiments were carried out at 77°K, but a few were made at 4°K. Temperature control was maintained by direct immersion of the sample in liquid nitrogen or liquid helium. Electrical connection to the crystals was made by use of indium contacts and the electric fields used were about 50 v/cm. A rocksalt prism monochromator in conjunction with a glowbar served as a source of infrared in the range from 1 to 10μ.

At 77°K the following results were obtained. Radiation in the 1μ wavelength region led to the well-known quenching of conductivity[10,11] produced by simultaneous

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[14] C. C. Klick, J. Opt. Soc. Am. **41**, 816 (1951).

[15] J. J. Lambe (to be published).

irradiation with light in the fundamental band. If the crystal was cooled to 77°K in the dark, no photoconductive response was observed on irradiation with infrared at wavelengths longer than 1μ. However, if the crystal was first illuminated with light in the fundamental absorption band and this visible illumination was then removed, infrared response was found in a region beginning about 1.8μ and extending out to about 6μ. The details of this are shown in Fig. 4. This band was determined to be the result of silver activation by performing similar experiments on unactivated CdS. It was noted that if the infrared was left on the crystal, the response gradually diminished. At 4°K this infrared response was not found, indicating, possibly, that these transitions are to excited states of the center from which thermal energy frees the charge carrier.

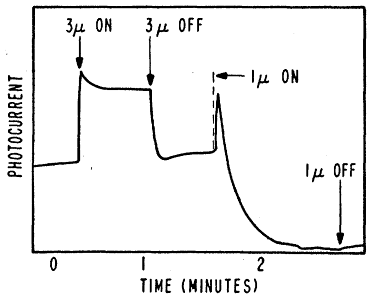

FIG. 5. Comparison of the action of 3μ irradiation and 1μ irradiation on photoconductivity of CdS(Ag) at 77°K.

The next step was to determine whether the infrared response was due to freeing of holes or electrons. In order to do this the following approach was followed. As previously mentioned, the well-known quenching action of 1μ irradiation has been ascribed to the liberation of holes. It is assumed that these holes then recombine with electrons in some manner, thus reducing the number of conduction electrons. It was decided, therefore, to compare the action of 1μ irradiation and 3μ irradiation on an existing photocurrent at 77°K. To do this a small amount of visible light was allowed to fall on the crystal and the crystal was irradiated first at 3μ and then at 1μ. The results of this experiment are shown in Fig. 5. It is seen that the 3μ irradiation produces a steady stimulation, while the 1μ irradiation brings about a complete quenching of the photocurrent. This indicates that the 3μ irradiation raises electrons into the conduction band rather than producing free holes. Moreover, it was noted that by irradiating at 1μ the 3μ response could be completely removed. It required re-exposure to visible light to restore the 3μ response.

More evidence will be presented in subsequent paragraphs regarding the difference in the effects of 1μ and 3μ irradiation, but at this point it may be well to summarize these experimental results in terms of the present model as is illustrated in Fig. 6. At 77°K, if the crystal has been exposed to light in the fundamental absorption band, there are filled electron levels about 0.4 ev below the conduction band due to silver activation. If the crystal has been cooled in the dark, these levels are empty; this will be discussed in more detail at the end of this section. In addition, there are the usual quenching levels the order of 1 ev above the valence band. If the crystal in this state were illuminated with infrared, no response should be observed, which is in agreement with experiment. If the crystal is illuminated with light of wavelength less than 5000 A, electrons will be raised into the conduction band, and many of them may be trapped at the luminescent centers. In addition, electrons in the quenching levels can combine with free holes in the valence band and thus the holes can be "trapped." Let the exciting illumination now be removed. Many of the electrons will remain in traps and also trapped holes will remain. If we now illuminate with 3μ infrared radiation, we can eject electrons from the luminescent centers and this will give rise to an infrared photoconductive response. If we illuminate with 1μ irradiation, this will free holes from the quenching centers which can then empty electrons from the Ag activator levels or recombine with free electrons. This should cause both the 3μ infrared photoconductive response to disappear as well as lower the conductivity due to irradiation in the fundamental band. Both these effects are observed. If the action of the quenching centers is due to the release of free holes, then the opposite effects, observed with the infrared centers introduced by the activator, should be due to the release of free electrons. It would appear extremely difficult to fit this conclusion into the Schön-Klasens model.

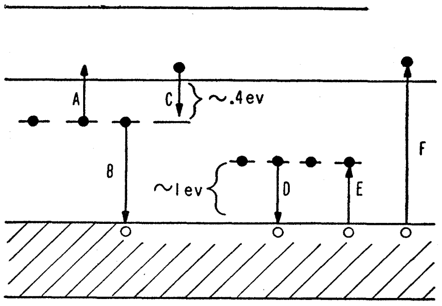

FIG. 6. Specific model proposed for CdS(Ag). Levels ~0.4 ev below conduction band result from silver activation. Levels 1 ev above valence band are normally present in CdS. *A:* Infrared excitation of trapped electrons (3μ region). *B:* Luminescent recombination of trapped electrons and free holes. *C:* Trapping of electrons. *D:* Trapping of holes. *E:* Freeing of trapped holes by excitation in 1μ region. *F:* Excitation.

In the model proposed here, it is assumed that the luminescent transition associated with the silver activation is due to the recombination of a hole in the valence band with an electron in the shallow activator level. It is clear then that irradiation in the quenching centers, which is believed to release free holes, should stimulate

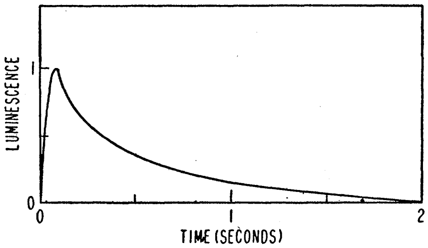

FIG. 7. Stimulation of luminescence in CdS(Ag) produced by 1μ irradiation.

luminescence if this model is to be consistent. To test this point the following experiment was carried out. A CdS(Ag) crystal was cooled to 77°K and irradiated with blue light. The light was removed and then the crystal was irradiated at 1μ. This caused a burst of orange luminescence which could be observed visually. A photomultiplier was used to record this burst and the result is shown in Fig. 7. Irradiation at 3μ did not produce any observable effect which is also in agreement with the model presented here.

Finally, it may also be noted that the bottom of the silver activation level is approximately 0.4 ev below the conduction band. The observed silver emission centers at about 2 ev so that these values are at least consistent with a total forbidden gap of 2.5 ev. The value of 0.4 ev from these infrared measurements is also in good agreement with the value of 0.5 ev obtained by Kröger, Vink, and van de Boomgaard[16] for silver activated cadmium sulfide from luminescence and absorption measurements.

The question arises as to why the silver activation levels should be normally empty as the crystal is cooled in the dark. The reason may be that on the basis of charge compensation, the introduction of silver without a coactivator should lead to missing sulfur ions at other parts of the crystal. These sulfur ion vacancies or other positively charged centers would form deep electron traps which may be filled by electrons from the shallow silver levels. This results in the behavior of silver activator levels as empty rather than as filled donor levels as the crystal is cooled in the dark to low temperature. In this case, irradiation in the fundamental band would first allow the shallow activator levels to be filled with electrons while the corresponding holes also become localized. After equilibrium has been reached, the luminescence mechanism would proceed as previously described. Before equilibrium can be reached, silver activator levels must be filled. This fact causes certain transient effects in luminescence and photoconductivity. These effects have been studied and are reported elsewhere.[15]

CONCLUSION

A model which assumes that the trapping of a hole, rather than an electron, leads to luminescence in sulfides activated by monovalent metals has been compared with experiment. Both this model and an older model account for such phenomena as the appearance of an impurity absorption band on the long-wavelength side of the fundamental band, effects of poisons, variation of luminescence color with temperature of doubly activated phosphors, and nonlinear effects in luminescence and conductivity. The explanation of the different decay times for luminescence and photoconductivity appears to be simpler on the new model. Finally, the observed stimulation of activator luminescence by irradiation in the quenching band and the increase in photoconductivity (rather than quenching) on irradiation in the $2-6\mu$ infrared band were predicted on the basis of the present model; it would appear to be difficult to explain these experiments with the older model.

ACKNOWLEDGMENTS

We should like to thank M. E. Bishop and David Patterson for their assistance in various aspects of this work.

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[16] Kröger, Vink, and van de Boomgaard, Z. physik Chem. **203**, 1 (1954).