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Electroluminescence and Thermoluminescence of ZnS Single Crystals

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Electroluminescence, thermoluminescence, and thermoluminescence under an applied voltage have been studied in ZnS single crystals. For electroluminescent crystals, the application of a constant electric field during thermoluminescence generally increases the intensity of the emitted light over the sum of the intensities due to the thermoluminescence and to the electroluminescence separately. A similar effect was observed during phosphorescence and during infrared stimulation. No such effects were observed on non-electroluminescent crystals. It was also found that an electric field can fill electron traps, but field emptying of traps did not appear to be important.

The current during the electroluminescence and during the thermoluminescence was measured simultaneously with the light emission. There was little correlation between current and thermoluminescence, but quite good correlation between current and the *additional* light resulting from a constant voltage during the thermoluminescence. These results suggest that some of the electrons released from traps contribute to the current and can cause impact excitation or ionization, but that others are not effective in this. Since both the current and the additional light are considerably higher during the high-temperature glow peak than during the low-temperature one, it appears that the electrons released from the deeper traps are more effective in these processes than those released from the shallower traps.

I. INTRODUCTION

ELECTROLUMINESCENCE in ZnS is commonly attributed[1,2] to impact ionization or excitation caused by high-energy conduction electrons. On the basis of this theory the electroluminescence intensity should depend on the number of conduction electrons available for starting the impact ionization, and one would except that an increase in the number of such electrons would increase the light emission. This effect has been reported on some phosphors for electrons generated by ultraviolet irradiation.[3] We have observed that if one supplies conduction electrons to electroluminescent ZnS crystals by release from traps, there also is such an effect. This work has already been briefly reported[4] for electrons freed during thermoluminescence, and further work has shown that the same effect can take place during phosphorescence and infrared stimulation. Thus, the method of release of the trapped electrons seems immaterial.

In the present work, the current during thermoluminescence and that during electroluminescence (the "dark current") were measured simultaneously with the light emission. On the basis of the impact excitation theory, one would expect a fairly close correlation between the light emission and the current, and this was indeed found for both the dc electroluminescence and for the additional light caused by applying a constant voltage during the thermoluminescence. However, there was little correlation between the current during thermoluminescence and the intensity of the thermoluminescence itself. Similar lack of correlation has been reported by Bube,[5] although in other cases there does appear to be fair correlation.[6]

II. EXPERIMENTAL METHOD

The work was carried out on single ZnS crystals grown by Kremheller by sublimation of ZnS powder.[7] In the main, three types of measurements were performed on the crystals: (1) the thermoluminescence, (2) the light and the current during thermoluminescence under an applied voltage, and (3) the temperature variation of the electroluminescence and of the dark current. These measurements were carried out between liquid nitrogen temperature (−196°C) and room temperature. The phosphorescence decay at −78°C and the infrared stimulation at −196°C with and without field were also investigated briefly.

The apparatus used in this work was the one described by Frankl,[2] except that a periscope arrangement was added in order to permit irradiation of the crystals. The crystal mounting and the method of taking measurements with half-wave voltages have also already been described.[2] For the measurements with constant voltages, the photomultiplier current was amplified and fed to a recorder, and the crystal current was measured by a microammeter.

The temperature variation of the electroluminescence was measured while the crystal was being cooled. Once the crystal was cool, it was excited for several minutes with either ultraviolet (mainly 3650 A) from a *BH*4

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[1] G. Destriau and H. F. Ivey, Proc. Inst. Radio Engrs. **43**, 1911 (1955); D. Curie, J. phys. radium **13**, 317 (1952); **14**, 510 (1953); L. Burns, J. Electrochem. Soc. **100**, 572 (1953); W. W. Piper and F. E. Williams, Phys. Rev. **81**, 151 (1952); W. W. Piper and F. E. Williams, British J. Appl. Phys. Suppl. **4**, *S*39–49 (1955); Zalm, Diemer, and Klasens, Philips Research Repts. **9**, 81 (1954).

[2] D. R. Frankl, Phys. Rev. **100**, 1105 (1955).

[3] D. A. Cusano, Phys. Rev. **98**, 546 (1955); F. E. Williams, Phys. Rev. **98**, 547 (1955).

[4] G. Neumark, Phys. Rev. **98**, 1546 (1955).

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

[6] G. F. T. Garlick and A. F. Gibson, Proc. Roy. Soc. (London) **A188**, 485 (1947); J. J. Dropkin, Final Report on ONR Project No. NR-015-207, 1954 (unpublished); I. Broser and R. Broser-Warminsky, British J. Appl. Phys. Suppl. **4**, *S*90 (1955).

[7] A. Kremheller, Sylvania Technologist **8**, 11 (1955).

TABLE I. Crystals examined.

Crystal No.	Electroluminescence[a]	Fluorescence color	Length between electrodes (mm)
1	Electroluminescent	Blue	2.8
2	Electroluminescent	Blue	1.4
3	Partly electroluminescent[b]	Blue-green	6.1
4	Nonelectroluminescent	Green	3.3
5	Electroluminescent	Blue-green	2.1
6	Electroluminescent	Blue	9.3
13	Electroluminescent	Blue	2.1
17	Electroluminescent	Blue	3.1
20	Electroluminescent	Blue	2.3
22	Electroluminescent	Blue	3.5
24	Electroluminescent	Blue	1.3
25	Nonelectroluminescent	Green	7
26	Nonelectroluminescent	Green	1.7
27	Electroluminescent	Blue	1.2
28	Nonelectroluminescent	Green	5.3
30	Electroluminescent	Blue	1.9

[a] The color of the electroluminescence was blue in all cases.

[b] Electroluminescent under half-wave excitation but not detectably so under dc (up to 2000 v).

lamp or by an electric field. The excitation was then stopped, the phosphorescence allowed to decay, and the crystal then warmed.[8] Without an applied field, this gives the thermoluminescence. With a field applied during the warming, one obtains what we shall refer to as "thermoluminescence with field."

A few measurements of fluorescence efficiency as a function of temperature were also taken. To prevent radiation from the *BH*4 lamp from reaching the photomultiplier, a 3650 A transmitting filter (Corning 5860) was inserted between the lamp and the crystal, and an ultraviolet cutoff filter (Schott *VG* 10) was inserted between the crystal and the photomultiplier.

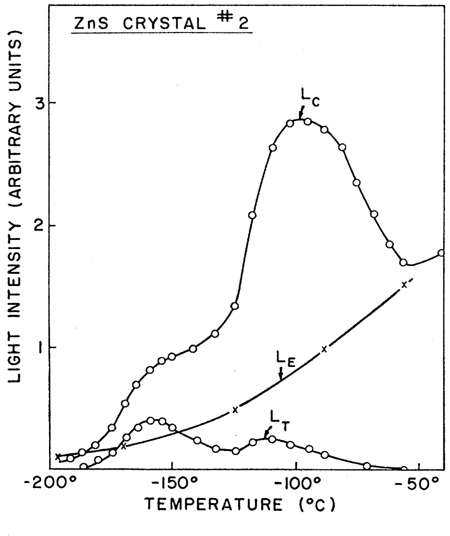

FIG. 1. Thermoluminescence with and without an applied voltage, and electroluminescence of a ZnS crystal; 800 v dc were applied.

III. EXPERIMENTAL RESULTS

The thermoluminescence, the light and the current during thermoluminescence with constant applied voltage, and the temperature variation under constant voltage of the dark current and of what we shall here refer to as the dc electroluminescence, were examined on the sixteen ZnS crystals listed in Table I. Some of these crystals were from the same growth experiments and had generally similar characteristics to the crystals discussed by Frankl.[2]

The light emission of a typical electroluminescent crystal is shown in Fig. 1, where L_C = intensity of the thermoluminescence with dc field (i.e., light emission due to the combined effect of the thermoluminescence and of an applied voltage), L_T = intensity of the thermoluminescence, and L_E = intensity of the dc electroluminescence. As in all thermoluminescence work, the instantaneous light emission (L_C and L_T in our case) is a function of both the temperature and the heating rate. In the present work, the same heating schedule was always used.

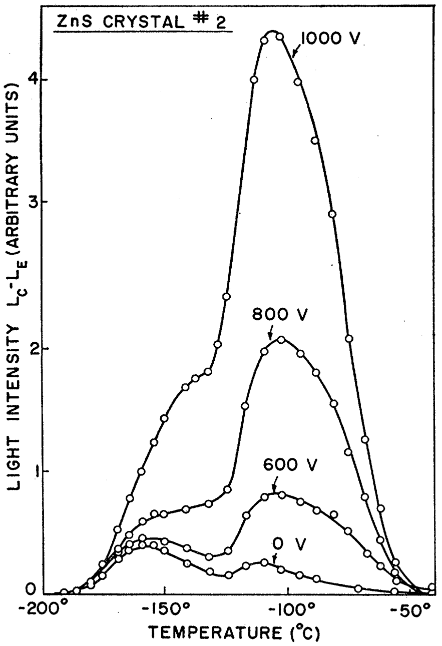

FIG. 2. Thermoluminescence with various dc voltages, with the electroluminescence subtracted out.

In order to emphasize the effect of the electrons released from the traps, L_E can be subtracted from L_C. Figure 2 shows a series of such "difference" curves at various voltages. These curves clearly show that the electrons released from the traps cause much more light in the presence of a field than without one, i.e., there is an "enhancement".

It should be emphasized that little or no enhancement was shown by any of the nonelectroluminescent crystals, or by crystal No. 3, which did not give dc

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[8] Since the apparatus was warmed only by the surroundings, the heating rate was not strictly linear; the average heating rate from −196° to −56°C (the region of thermoluminescence) was ≈7°/min.

electroluminescence. However, out of the eleven electroluminescent crystals nine showed $(L_C-L_E)>2L_T$, at least at higher applied voltages and higher temperatures. In this connection, it should be noted that the enhancement was generally higher at the higher temperatures. At the lower temperatures, below $\approx -150°$C, (L_C-L_E) was sometimes slightly less than L_T; however, any such "quenching" effect was always small in comparison to the changes obtained during good enhancement. Similar slight quenching was also sometimes obtained on the nonelectroluminescent crystals.

To test for ultraviolet emission, an ultraviolet transmitting filter (Corning 9863) was inserted between some of the crystals and the photomultiplier during the electroluminescence and during the thermoluminescence with field. No signal was obtained under these conditions. The detailed spectral distribution of the half-wave electroluminescence of similar crystals has already been reported.[2]

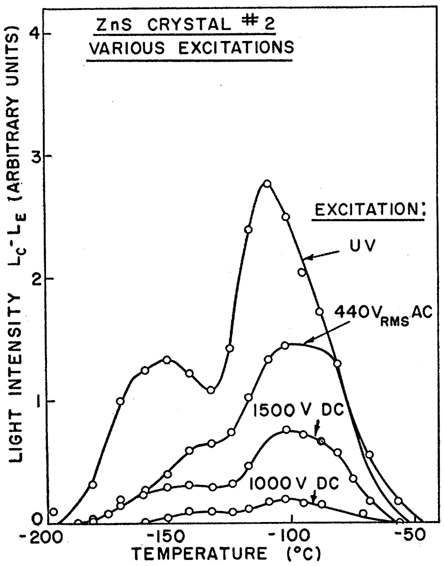

FIG. 3. Thermoluminescence with 1000 v dc after the subtraction of the electroluminescence, with the measurements taken after various low-temperature excitations.

Measurements of the fluorescence intensity as a function of temperature were taken on crystals No. 4 and No. 20. The intensity was found to vary by not more than 40% in the region of thermoluminescence (−196°C to −56°C).

In a few cases, the thermoluminescence with field was obtained by using field excitation instead of ultraviolet excitation. Either an ac or a dc electric field was applied for 10–20 minutes while the crystal was cool, and the crystal then warmed under a given field. Figure 3 shows the resultant difference curves for various excitation fields.

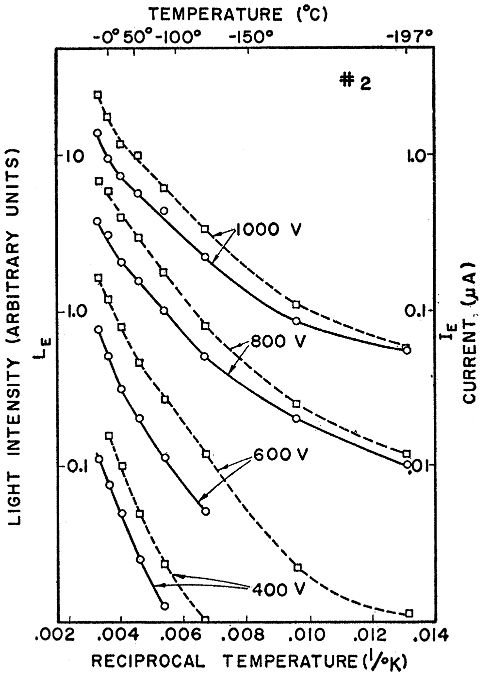

FIG. 4. The dc electroluminescence (–○–) and the corresponding current (–□–) at various voltages.

The method of trap emptying was also varied. The phosphorescence decay at −78°C of crystal No. 17 and the infrared stimulation at −196°C of crystal No. 20 were examined with and without field. In both cases, the emission intensity under the combined action of the field and of the trap emptying was considerably higher than the sum of the intensities due to the individual effects.

The electroluminescence intensity and the dark current, I_E, of crystal No. 2 at various voltages are shown as functions of the reciprocal temperature on Fig. 4. It can be seen that both vary very similarly. For other crystals (Fig. 5), the correlation between the two is not always quite as good, but there nevertheless is still a fairly close correspondence.

If one examines the current due to thermal trap emptying one finds that there is not much correlation with the intensity of the thermoluminescence, as shown on Fig. 6. Here I_C stands for the current under the combined action of field and trap emptying, and corresponds to L_C. Since we are again interested in the effect of the electrons released from traps, L_E and I_E were subtracted for crystals No. 1 and No. 27; for crystals No. 3 and No. 4 both were insignificant.

A few measurements with 60-cycle half-wave rectified sinusoidal voltage and full 60-cycle sinusoidal voltage were also taken. The behavior of the electroluminescence was rather complex, and will be discussed only briefly. With decreasing temperature, the maximum intensity of the electroluminescence peaks sometimes decreased monotonically, and sometimes showed maxima and minima. The detailed behavior depends on the crystal

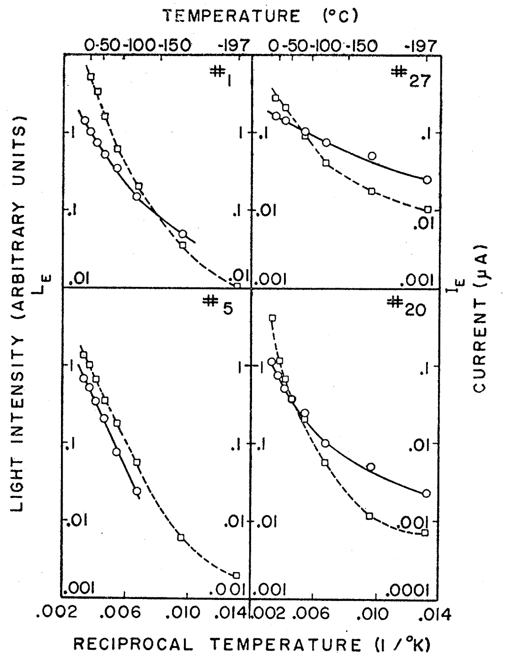

FIG. 5. The dc electroluminescence (–○–) and the corresponding current (–□–) for various crystals; crystal No. 1 at 1500 v, and No. 5, 20, and 27 at 1000 v.

and the voltage, as well as on the peak being examined; for crystal No. 2, under half-wave excitation of 1.4-kv peak voltage, the 90° peak decreased monotonically, but the 150° did not. Another interesting feature, one that is in sharp contrast with the dc behavior, is that low temperature ultraviolet excitation frequently has relatively little effect on the light emission and current. For example, with crystal No. 22 under half-wave excitation of 1.4-kv peak voltage, the peak light emission and the peak current on warming after ultraviolet excitation did not differ by more than 20% from the corresponding values obtained on cooling.

IV. DISCUSSION

A. General Conclusions

One of the main conclusions of this work is that in electroluminescent crystals at least some of the electrons released from traps frequently cause additional emission in the presence of a dc field. If one assumes impact excitation or ionization by these electrons, this result can easily be understood. The question of whether this excitation takes place at barriers or throughout the crystal was not examined. However, Frankl has found that the light distribution during electroluminescence frequently seems to be quite uniform, which presumably means that macroscopic barriers are not essential for excitation[2]; this view tends to be confirmed by the observation that the potential distribution across at least some electroluminescent crystals appears to also be reasonably uniform.[9]

It should further be noted that the nonelectroluminescent crystals examined gave no enhancement, although there was a current during the thermoluminescence. Thus, the absence of impact ionization or excitation is here due to something other than the absence of conduction electrons.

The fact that a field-enhanced brightness is obtained during thermoluminescence, phosphorescence, and infrared stimulation shows that the method of release of the trapped electrons is relatively immaterial. Field release of trapped electrons, whether or not partially present, does not seem to play an important role in the present work; as clearly shown on Fig. 2, there is enhancement as long as there is regular thermoluminescence, which indicates that at least some of the traps remain filled even in the presence of an applied voltage. Also, if field ionization of traps took place, one might expect a burst of light upon applying a field after the ultraviolet irradiation; however, it was found that there is either no such burst or only a very slight one.

Further, as reported earlier,[4] one can conclude that an electric field can fill traps, although not necessarily to the same extent as ultraviolet excitation (see Fig. 3). Johnson, Piper, and Williams have recently also reported such trap filling.[10] Apparently, under half-wave and ac fields this filling of traps can proceed far enough so that low-temperature ultraviolet excitation sometimes no longer greatly affects the electroluminescence

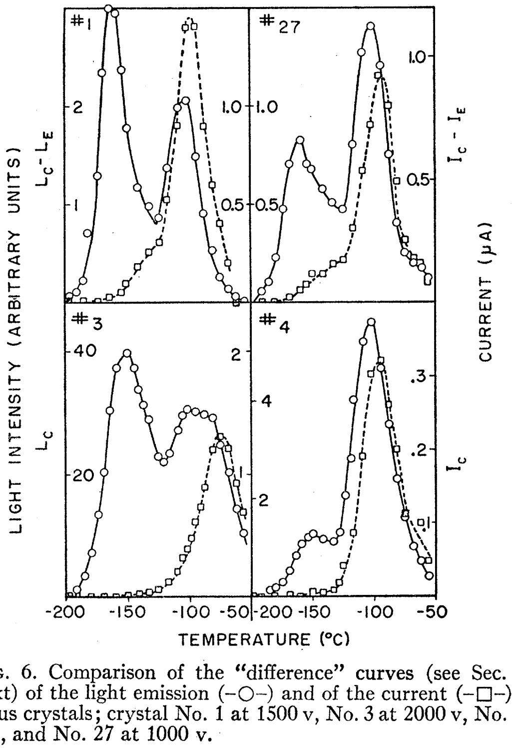

FIG. 6. Comparison of the "difference" curves (see Sec. III of text) of the light emission (–○–) and of the current (–□–) for various crystals; crystal No. 1 at 1500 v, No. 3 at 2000 v, No. 4 at 300 v, and No. 27 at 1000 v.

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[9] A. Lempicki, J. Opt. Soc Am. (to be published).

[10] Johnson, Piper, and Williams, Abstracts of the Electrochemical Society Spring Meeting, 1955 (unpublished).

or the current. On the other hand, the proportion of traps filled during dc electroluminescence seems very small; for crystal No. 2, the light emission due to trap filling by 1000 v dc, which was one of the higher voltages applied to crystals showing good enhancement, was less than 5% of that due to trap filling by the ultraviolet irradiation (see Fig. 3).

Both the results showing the filling of traps during electroluminescence and those showing the enhancement of the electroluminescence by electrons released from traps are consistent with results reported by Gobrecht, Hahn, and Gumlich,[11] who report obtaining pronounced differences in electroluminescence upon cooling and then upon rewarming their phosphors. However, they did not measure ultraviolet-excited thermoluminescence with field, nor did they measure current.

B. Details of the Enhancement and of the Current Associated with the Thermoluminescence

As mentioned in Sec. III, and as can be seen from Fig. 2, the enhancement is usually low at the lower temperatures, and increases with increasing temperature. It is interesting to note that the ratio of the current to the light intensity during thermoluminescence behaves similarly; as can be seen on Fig. 6, the current is very low during the low-temperature glow peak, and increases rapidly around the beginning of the high-temperature glow peak.

The variation of the current with respect to the thermoluminescence intensity can be due either to a change in the effectiveness of the released electrons as current carriers, or to a change in the efficiency of the light emission process. The latter is unlikely for two reasons: (1) the temperature variation of the fluorescence efficiency, where examined, was not nearly as pronounced as that of the current *vs* the light emission, and (2) relatively good correlation is found between the temperature variation of the electroluminescence and that of the dark current, and this would not be likely if there were pronounced changes in the efficiency of the emission process.

It thus seems probable that there is a change in the effectiveness of the released electrons as current carriers. Such a change would also explain the temperature dependence of the enhancement: if an electron is not effective as a current carrier it means that it is not appreciably displaced by the field and thus it cannot gain sufficient energy for impact excitation or ionization. If this is indeed the case, and if the temperature variation of factors such as electron scattering mechanisms and fluorescence efficiency is slight compared with that of the effectiveness of the electrons, then one would expect that the temperature dependence of the additional light produced by the effective electrons would be similar to that of the current. The light caused by impact excitation due to such effective electrons is just $L_C-L_T-L_E$, and this quantity is compared to the current for cases of high enhancement in Fig. 7. The correlation is seen to be excellent. Here, for crystals No. 20 and No. 24 L_E and I_E were negligibly small, and therefore not subtracted.

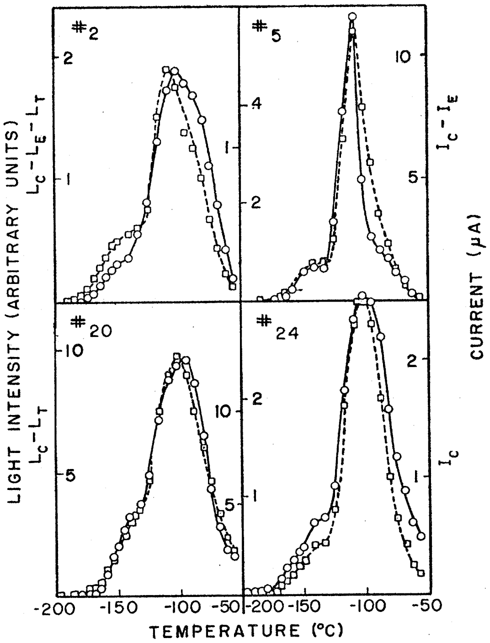

FIG. 7. Comparison of the additional light (–○–) due to the release of trapped electrons, ($L_C-L_T-L_E$), with the current (–□–) due to the release of trapped electrons (I_C-I_E); crystal No. 2 at 800 v, No. 3 and 5 at 1000 v, and No. 20 at 400 v.

This still leaves open the question of the cause of the change in the effectiveness of the released electrons. One possibility is that the low temperature trap together with the activator forms a localized center so that the electrons for the most part do not reach the conduction band. Localized centers have recently been proposed by Frankl[2] to explain the time dependence of the half-wave electroluminescence; however, the present centers cannot be of the same type since they release electrons also in the presence of a field, while in Frankl's model the centers are stabilized by a field. It should be noted that even if the low-temperature traps are in localized centers some of the electrons nevertheless reach the conduction band, since there is both some current and some enhancement in the low-temperature thermoluminescence peak.

However, localized centers are certainly not the only possibility. If, for example, the crystals had small regions of potential fluctuations, only those electrons which could get over the barriers caused by the fluctuations would contribute to the current[12] and thus to the enhancement. As the temperature is increased, the

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[11] Gobrecht, Hahn, and Gumlich, Z. Physik **136**, 623 (1954).

[12] For a similar hypothesis for PbS, see Mahlman, Nottingham, and Slater, *Proceedings of the Atlantic City Photoconductivity Conference, 1954* (John Wiley and Sons, Inc., New York, 1955).

average electron energy would increase, and this would cause a larger fraction of the electrons to get over the barriers. It should be noted that models involving a series of barriers have already been postulated for ZnS crystals,[2,13] as well as for diamond[14] and lead sulfide.[12,15] Or, the increase in current and enhancement could also be the results of an increase, with increasing temperature or increasing trap-emptying, of either the field strength in the regions of trap emptying, or of the electron lifetime.

C. Temperature Variation of the Electroluminescence and of the Dark Current

As can be seen from Figs. 4 and 5 the dc electroluminescence and the dark current behave quite similarly with respect to temperature. Both increase rapidly with increasing temperature. This increase is not linear on a $\log L_E$ and $\log I_E$ *vs* reciprocal temperature plot except for a very small temperature region. This is hardly surprising, however, since no account has been taken of the temperature variation of the mobility, and since the current and light were measured with a constant applied voltage which, in the presence of barriers, does not necessarily give a constant field in any given region. These two factors also make it difficult to interpret the cause of the linear portion that does exist. Two possibilities are that it is due either to electrons being released from impurities, or to electrons getting over barriers. If it is the latter, it would be relatively easy to understand both the variations from crystal to crystal (see Fig. 5), and a decrease in slope with increasing voltage observed for some of the crystals. Such a decrease might come about if the "activation" energy is due to barriers, and if these barriers are lowered by the presence of a larger amount of free charge. The most pronounced example of this decrease in slope occurs for crystal No. 2 (Fig. 4), where there is a decrease from 0.1 ev at 400 v to 0.04 ev at 1000 v.

As mentioned in Sec. III, the temperature variation of the half-wave and ac electroluminescence is rather complex, and we will therefore not consider it in detail here. Since electron traps become filled during this electroluminescence, the trap filling and emptying processes probably play a role; however, so may other factors. Various hypotheses have already been proposed to account for the temperature dependence of the ac electroluminescence. One, by Williams,[16] assumes increased electroluminescence due to the release of trapped electrons, and thus is consistent with our dc results (although he assumes field ionization of traps which, as discussed in Sec. IV. A, does not seem dominant under dc voltages). Other hypotheses have been proposed by Johnson, Piper, and Williams in an earlier paper,[10] as well as by Haake[17] and by Alfrey and Taylor[18]; the effects proposed by them may be important under certain conditions or for certain phosphors, but they do not seem necessary for explaining the main features of the present dc results.

V. SUMMARY

It has been shown that electrons released from traps will, in the presence of a dc field, cause an enhanced light emission in most of the electroluminescent crystals tested. This enhanced emission is closely related to the current and can be explained by assuming impact excitation or ionization caused by some of the electrons released from the traps. Despite the presence of a current, an enhanced emission was not found for the nonelectroluminescent crystals we tested.

It was found that both the enhancement and the current due to the release of trapped electrons increased with increasing temperature. This increase may be associated with the presence of small, probably microscopic barriers in the crystals. Such barriers would also explain some of the characteristics of the temperature dependence of the dc electroluminescence. It is thus noteworthy that both these phenomena can be explained by the same theory, although this of course does not exclude the possibility that the two are independent.

VI. ACKNOWLEDGMENTS

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[13] E. E. Loebner and H. Freund, Phys. Rev. **98**, 1545 (1955); E. E. Loebner, Abstracts of the Polytechnic Institute of Brooklyn Symposium, 1955 (unpublished).

[14] G. H. Wannier, Phys. Rev. **76**, 438 (1949).

[15] H. M. James, Science **110**, 254 (1949).

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[18] G. F. Alfrey and J. B. Taylor, Proc. Phys. Soc. (London) **B68**, 775 (1955).