

Infrared Sensitivity of the ZnS:Cu:Co Phosphor*†

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(Received September 11, 1961; revised manuscript received January 16, 1962)

The infrared-sensitive photoconductive and luminescent response of the ZnS:Cu:Co phosphor has been studied in the temperature range from -178° to 250°C . At -178°C the green luminescence and the photoconductivity are both stimulated by the infrared radiation peaking sharply at $1.2\ \mu$. At 30°C , infrared irradiation produces the customary quenching of the luminescence but an enhancement of the photoconductivity. The spectral response of these consists of two bands peaking at 0.8 and at $1.3\ \mu$. At intermediate temperatures, the total infrared response is very complex and this has been shown to be due to the simultaneous presence of quenching and stimulation.

The infrared sensitivity can be resolved in terms of two basic electronic transitions. The first is from a deep copper storage center to the conduction band and produces the low-temperature stimulation. The second, of the type first described by Schön and Klasens, produces quenching and is from the valence band to an empty copper luminescent center. Filled cobalt traps are found to play an essential role in this quenching process. An energy band scheme is proposed which is consistent with the observed effects.

INTRODUCTION

THE luminescence of the ZnS:Cu:Co phosphor is known to be sensitive to infrared (ir) radiation. At room temperature the fluorescence is quenched¹⁻³ while at liquid nitrogen temperature the phosphorescence is stimulated.⁴ The work to be reported in this paper was undertaken to clarify the nature of the electronic transitions associated with this sensitivity. For this purpose we have studied the fluorescence, the

stimulated phosphorescence and photocurrent, and the thermoluminescence glow curves as functions of intensity and wavelength of ir radiation in the temperature range from -178° to 250°C .

The results of these studies have indicated that the ir sensitivity can be understood in terms of two basic electronic transitions. One is from a deep copper storage center to the conduction band and is responsible for the low-temperature stimulation. The other, which produces the quenching, requires thermal activation and is from the valence band to an empty copper luminescent center followed subsequently by hole migration and recombination at filled cobalt traps.

PHOSPHOR PREPARATION AND EXPERIMENTAL APPARATUS

Details of the phosphor preparation, of the ($3650\ \text{\AA}$) uv and (0.7 to $2.0\ \mu$) ir-excitation sources, and of the measurement of the green luminescence of the phosphor at different temperatures, have been given in an earlier paper.⁵ The photoconductivity of the phosphor was measured with a dc electrometer amplifier⁶ which included a bucking circuit for the dark current.

While the luminescence measurements involved no particular problem, the photoconductivity measurements were complicated by the presence in the phosphor of two space-charge effects.^{7,8} One was the build-up of a space charge during irradiation and application of an external field caused by barriers at the electrodes or between phosphor grains. The other was the formation of a "frozen-in" space charge caused by the trapping of photoproduced charge carriers as they drift toward their respective electrodes. Both these effects cause a

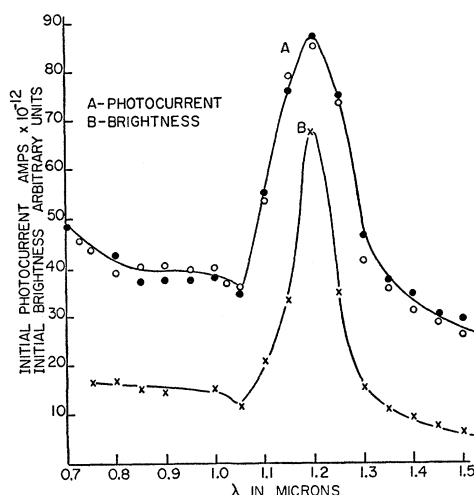


FIG. 1. Wavelength dependence of the ir-stimulated emission and the ir-stimulated photocurrent at -178°C for ZnS:Cu:Co. The uv excitation state of the phosphor is reproduced for each ir reading.

* This paper is based on part of a thesis submitted by Bernard Goldstein in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

† The work described in this paper was supported by the Office of Naval Research, Contract N6 onr 26313.

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¹ R. Coustal, *Compt. rend.* **190**, 1403 (1930).

² N. Melamed, *J. Electrochem. Soc.* **97**, 33 (1950).

³ H. Klasens and W. Hoogenstraaten, *J. Electrochem. Soc.* **100**, 366 (1953).

⁴ G. Garlick and D. Mason, *J. Electrochem. Soc.* **96**, 90 (1949).

⁵ B. Goldstein and J. J. Dropkin, *J. Electrochem. Soc.* **106**, 682 (1959).

⁶ G. Gabus and M. Poole, *Rev. Sci. Instr.* **8**, 196 (1937).

⁷ J. J. Dropkin, final report, "Photoconduction in Phosphors," U. S. Navy Contract N6 onr 26313.

⁸ J. J. Dropkin, *Proceedings of the Symposium on Role of Solid-State Phenomena in Electric Circuits*, Polytechnic Institute of Brooklyn, 1957 (Polytechnic Press, Polytechnic Institute of Brooklyn).

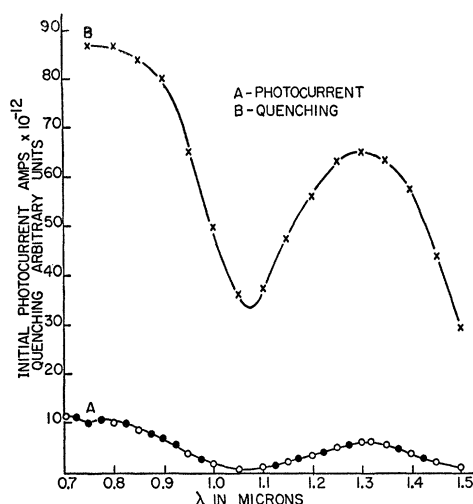


Fig. 2. Wavelength dependence of the ir fluorescence quenching and ir-stimulated photocurrent at 35°C for ZnS:Cu:Co . The ir photocurrents are taken in the absence of uv after a fixed period of excitation and phosphorescent decay.

decrease of photocurrent with time and result in a measurement error. An attempt was made to minimize the error introduced by these effects by using as the photocurrent the sum of the maximum "forward" current taken with external field applied, and the maximum "reverse" current taken with external field removed and phosphor shorted.⁹ This procedure yielded total photocurrents which followed Ohm's law at all temperatures for both uv and ir irradiation even though the initial or "forward" photocurrent did not. No accurate estimate of the absolute error in the true photocurrent was made and these measurements were not used for detailed quantitative analyses. Rather, they were used almost solely for determining the wavelength dependence of the photoconductive responses in order to relate them to associated ir-induced changes in the luminescence.

RESULTS

1. Primary Effects of IR Irradiation

Figures 1 and 2 show the luminescent and photoconductive effects produced by ir irradiation at -178° and at 35°C . In these, and in all subsequent measurements unless specifically stated otherwise, each ir measurement was made after bringing the phosphor into equilibrium with a constant level of uv excitation. The ir stimulation is measured with the uv off; the ir quenching is measured with the uv on. At -178°C there is a strong peak at $1.2\ \mu$ in the stimulation of the green luminescence. At 35°C the customary quenching spectrum is observed which is found for all ZnS phosphors containing copper² with peaks at 0.8 and $1.3\ \mu$. Both the low-temperature stimulation and the

room temperature quenching are accompanied by enhanced photoconductivity which is clearly associated with the changes in emission.

The dominance of the quenching process at room temperature and its absence at -178°C indicate that some thermal energy is required for this process. Stimulation, on the other hand, either requires none or very much less than that of quenching. This, plus the difference between the stimulation and quenching spectra shown in Figs. 1 and 2, suggest that the electronic transitions associated with quenching and stimulation are different. Experiments involving the addition of CdS to the host lattice to form solid solutions of ZnCdS further substantiate this. The addition of only 10% CdS causes the $1.2\text{-}\mu$ stimulation peak to disappear but leaves the positions of the quenching bands unchanged.

In subsequent sections we present and discuss results which clarify the nature of the stimulation and quenching transitions.

2. Nature of the IR Stimulation

If the phosphor is excited with uv to saturation at -178°C , heated to temperatures above 300°C , then recooled to -178°C , no $1.2\text{-}\mu$ stimulation is found; uv re-excitation is required to restore it. In addition, the magnitude of the stimulation is, initially, dependent on the time of uv excitation. This indicates that the principal source of the stimulation is an electron storage center with an optical ionization energy of about 1 eV.¹⁰ This center is associated specifically with copper since it has been shown that only with copper as an activator does the $1.2\text{-}\mu$ band appear.⁴ The stability of this center is demonstrated by a very slow spontaneous decrease in the initial ir photocurrent at -178°C , and by the fact that the phosphor must be heated to about 30°C before any decrease in ir photocurrent on subsequent recoiling to -178°C is seen. The phosphor must be irradiated with intense $1.2\text{-}\mu$ ir at 250°C in order to exhaust the storage properties completely.

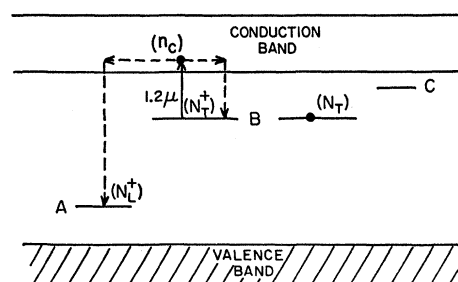


Fig. 3. Simplified energy level diagram for the low-temperature ir stimulation process. Levels A are the empty luminescent centers. Levels B are the occupied and empty $1.2\text{-}\mu$ storage states. Levels C are shallow traps.

⁹ This procedure also depolarized the phosphor between readings.

¹⁰ It has been shown in an earlier publication that the shallow traps, *per se*, do not contribute significantly to the $1.2\text{-}\mu$ stimability. (See reference 5.)

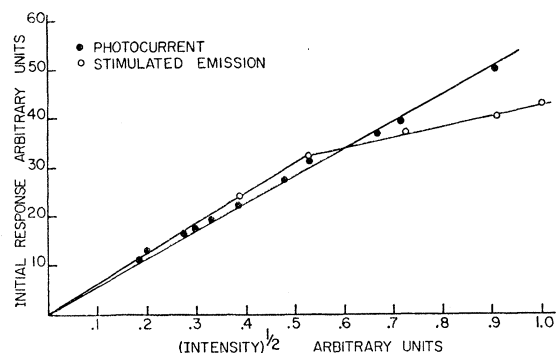


FIG. 4. Intensity dependence of the initial ir-stimulated emission and ir-stimulated photocurrent for ZnS:Cu:Co at -178°C .

3. Kinetics of the IR Stimulation

Referring to the simplified energy level diagram shown in Fig. 3, the kinetics of the ir-stimulated luminescence and photoconductivity are determined by the number of electrons in the conduction band n_e , the number of empty luminescent centers N_L^+ , the number of filled ir storage states N_T , the number of empty ir storage states N_T^+ , the number of shallow traps and the relative capture cross sections of these levels for electrons.¹¹ The levels of Fig. 3 may be attributed as follows. Levels *C*, the shallow traps, are associated with the coactivator which is Cl in this case.¹² The levels *A* and the levels *B* are associated with the Cu luminescent center.⁴ We suggest that the levels *B* exist only for the case when the luminescent center is empty, i.e., ionized, and that therefore $N_L^+ > N_T^+$ whenever $N_T \neq 0$. This is in accord with the work of Prener and Williams¹³ in support of their model of the Cu luminescent center in ZnS:Cu:Cl formed by Cu substitutionally forming covalent bonds in the ZnS lattice by taking an extra electron from an associated Cl which is replacing a sulfur. On this basis, a precondition for trapping an electron by the Cu center in the deep traps of levels *B* would be the ionization of the Cu center.

In the following discussion, two additional factors should be noted. The first is that for measurements at -178°C of the stimulability of a fully uv-excited phosphor, the shallow traps are filled and play no part.⁵ The second is that N_L^+ , the number of empty luminescent centers, is greater than either n_e or N_T since all electrons in the conduction band and traps (both deep and shallow) originate from the luminescent centers for 3650-Å excitation.

If A_L is the capture cross section of the empty luminescent center, and A_T the capture cross section of the empty storage center, the kinetics of the ir stimulation will be determined by the relative size of $A_L n_e N_L^+$

and $A_T n_e N_T^+$. The following experimental results indicate that $A_T \gg A_L$.

The initial ir-stimulated luminescence and photoconductivity both vary approximately as the square root of the ir intensity. The experimental results are shown in Fig. 4. Since the initial luminescence is proportional to n_e (the initial value of N_L^+ is constant for constant excitation conditions), and the photocurrent is always proportional to n_e the initial brightness and the initial photocurrent should vary in the same way. The significance of the square root dependence is that of a bimolecular process i.e., that the dominant process determining the variation of n_e with ir intensity is retrapping.¹⁴

Retrapping in the storage center can also be seen from the behavior of the forced decay of the stimulated emission and photocurrent while under steady ir irradiation. The forced decay of the stimulated photocurrent is extremely slow even though the forced decay of the stimulated emission is rapid. The latter is shown in Fig. 5(A). During the first 30 sec of the decay the emission has dropped to 10% of its initial value. The photocurrent at this time is still at 90% of its initial value. The large drop in luminescence, then, is due to nonluminescent retrapping, i.e., $A_T n_e N_T^+ \gg A_L n_e N_L^+$. If in accord with our suggestion, $N_L^+ > N_T^+$, we would have $A_T \gg A_L$.

The relative effect of retrapping and luminescent recombination is also shown from the results of irradiating the phosphor simultaneously with uv and ir. If the phosphor is excited with uv to an equilibrium level of fluorescence and is then irradiated with 1.2-μ ir, the fluorescence is first stimulated and then decays to the

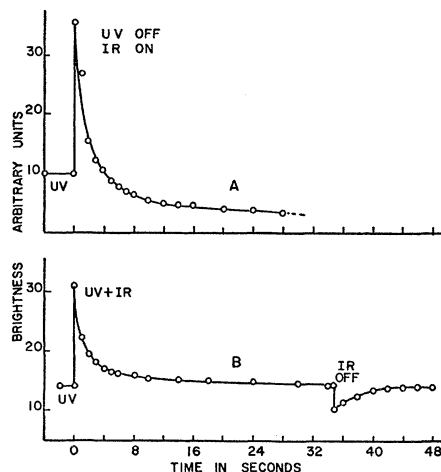


FIG. 5. A: Decay of the ir-stimulated emission of ZnS:Cu:Co at -178°C under constant 1.2-μ irradiation. B: Uv fluorescence of ZnS:Cu:Co at -178°C with and without simultaneous 1.2-μ irradiation.

¹¹ The possibility of holes in the valence band playing a part in this process is discussed below and rejected.

¹² W. Hoogenstraaten, J. Electrochem. Soc. **100**, 356 (1953).

¹³ J. S. Prener and F. E. Williams, J. Electrochem. Soc. **103**, 342 (1956).

¹⁴ The flattening of the brightness curve relative to the photocurrent curve may be due to our assumption of constant N_L^+ . This number can be appreciably decreasing during the time of a reading at the higher ir intensities.

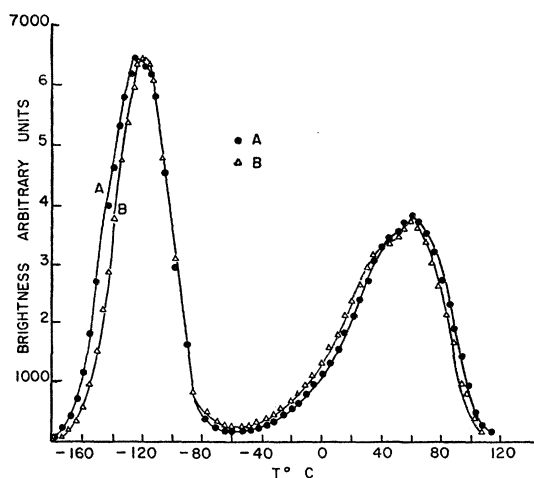


FIG. 6. Thermoluminescence glow curves for ZnS:Cu:Co excited at -178°C . A: Excited by 30 min of uv. B: Excited by 29 min of uv followed by simultaneous uv and $1.2\text{-}\mu$ ir for 1 min.

original uv level in less than one minute as shown in Fig. 5(B). That this decay in the stimulability is not due to retrapping in additional empty shallow traps can be seen from Fig. 6 where simultaneous uv and ir irradiation produces essentially the same glow curve as that due to uv alone. Therefore the decay of the stimulability must be due to the emptying of the $1.2\text{-}\mu$ storage center. If, after the stimulated emission reaches its previous level the ir is removed, the fluorescence drops sharply and then again returns to its original uv level [see Fig. 5(B)]. As soon as the ir is removed, the empty storage centers N_T^+ and the empty luminescent center N_L^+ compete for n_c the conduction band electrons being supplied by the uv. The sharp drop in the emission and the slow rise to equilibrium indicate again that $A_T n_c N_T^+ \gg A_L n_c N_L^+$.

4. Onset of IR Quenching

As the temperature is raised from -178° to 30°C the phosphor changes from ir-stimulable to ir-quenching. At -70°C quenching has already begun to supplant stimulation. This is shown in Fig. 7. Here, the phosphor has been brought to an equilibrium level of fluorescence and then irradiated with different wavelengths of ir. First, stimulation is produced, and after several seconds a new equilibrium is established at lower values of fluorescence. The quenching spectrum at -70°C is the same as that found at room temperature but with a narrower $0.8\text{-}\mu$ peak. The complexity of the stimulation spectrum is due, at least in part, to the strong action of the quenching process. At room temperature the stimulation has disappeared and only quenching is observed.

5. IR Quenching and the Cobalt Traps

We have found as a result of glow curve experiments that the cobalt traps in the ZnS:Cu:Co phosphor play

an integral role in the quenching process. The normal thermoluminescence glow curve of the phosphor, shown in Fig. 6, curve A, has two peaks. One is at low temperature representing a localized distribution of traps due to copper, and one is at 60°C representing traps due to cobalt.⁵ At room temperatures, where ir quenching is dominant, the copper traps are empty and cannot hold electrons. However, the cobalt traps are stable and can. Ir irradiation at 0°C prior to a glow curve commencing at that temperature empties these cobalt traps. The wavelength dependence of this effect is shown in curve A, Fig. 8, in which we have plotted percent decreases in cobalt glow peak area vs wavelength. In addition, we have also measured the wavelength dependence of the delay in the rise time of the uv fluorescence at room temperature due to pre-irradiation with ir. The pre-irradiation empties cobalt traps which can then capture a significant fraction of the excited electrons during the initial stages of excitation. These results are plotted in curve B, Fig. 8. Comparing these curves with those in Fig. 2, it can be seen that the wavelengths of ir most effective for quenching are also most effective in depopulating the cobalt traps. Thus, the basic ir-quenching transition must also account for the emptying of the cobalt traps.

DISCUSSION

In this section we discuss the sets of electronic transitions producing the ir sensitivity in the ZnS:Cu:Co phosphor in terms of the energy-band scheme shown in Fig. 9. We have included only those levels and transitions whose existence has been indicated directly by our experimental results. For the ir quenching we have assumed a Schön-Klasens^{15,16} model in

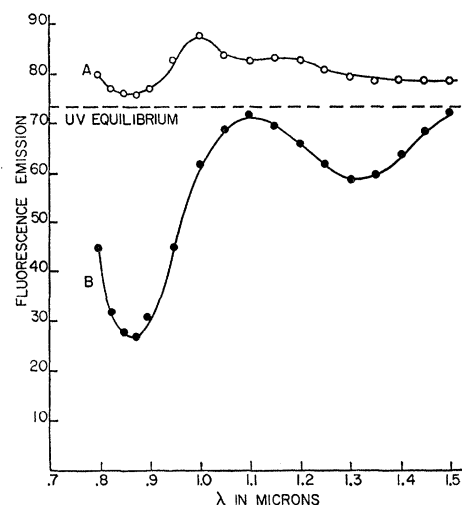


FIG. 7. Changes in fluorescence of ZnS:Cu:Co produced by ir irradiation at -70°C . A: Initial stimulated emission. B: New equilibrium level of fluorescence.

¹⁵ M. Schön, Z. Physik **119**, 463 (1942).

¹⁶ H. Klasens and M. Wise, Nature **158**, 483 (1946).

which the primary transition is that of an electron from the valence band to the empty Cu luminescent center with subsequent hole migration to the cobalt center. This assumption is based in part on the wavelength dependence of both quenching and photoconductivity (Fig. 2), in part on the fact that the quenching bands are unchanged with the addition of CdS in amounts sufficient to lower the conduction band by 0.3 eV relative to the valence band, and finally on the fact that recent measurements have shown a positive net sign for the charge carriers produced in ZnS:Cu phosphors by ir radiation at the wavelengths which cause quenching.¹⁷

In Fig. 9, levels *A*, *B*, and *C* are, respectively, luminescence recombination centers, 1.2- μ storage centers, and shallow traps responsible for the low-temperature glow peak. These are all due to copper or a copper complex. Level *D* is the shallow trap due to cobalt and is responsible for the 60°C glow peak. The ir-stimulation transition is simply described by transition 1 from level *B* to the conduction band. Initially, the excited electrons may either recombine at *A* resulting in stimulated emission, or be trapped at *C* and *D* resulting in enhanced glow curves, or be retrapped at *B* which is most

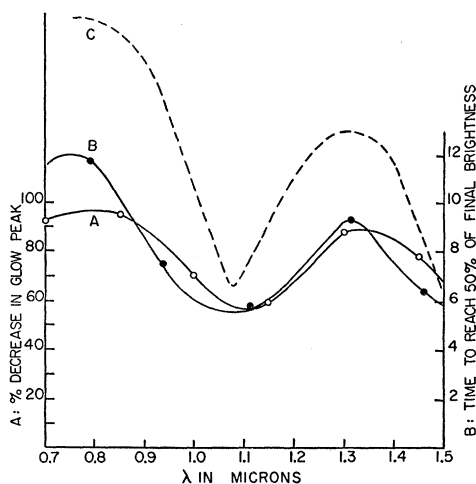


FIG. 8. Wavelength dependence for ZnS:Cu:Co of the decrease in the cobalt glow peak area (curve A), and of the delay in the uv fluorescence rise time (curve B), both due to previous ir irradiation. Normal rise time is 5.1 sec. Curve C is an ordinary ir quenching spectrum at 35°C included for comparison.

¹⁷ U. K. Nymm and L. I. Uibo, Trans. Inst. Phys. and Astron. Estonian S.S.S.R. 4, 124 (1956).

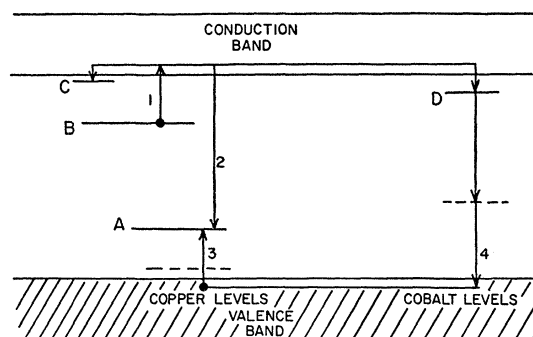


FIG. 9. Energy-level diagram for the ir sensitivity of the ZnS:Cu:Co phosphor. Levels *A* are empty luminescent centers. Levels *B* are 1.2- μ storage states. Levels *C* and *D* are the shallow traps due to copper and cobalt which produce the glow curves. Transition 1 is the basic ir stimulation process at -178°C. Transitions 3 and 4 form the basic ir quenching process at room temperature.

probable. Apparently, the transition from *B* to *A* directly is forbidden, since in all cases enhanced photoconductivity results. Then, as the phosphor is raised to intermediate temperatures, the thermal energy required for the quenching transition becomes available and the total ir response becomes more complex. At room temperature the quenching transition 3 has become predominant. This is accompanied by an enhanced photoconductivity caused by the holes. The holes migrate through the crystal and are captured by the filled cobalt traps, transition 4, accounting for the depletion of the cobalt traps which accompanies the quenching. If the cobalt traps were not filled, then the holes might re-ionize the copper luminescent centers. Thus, the filled cobalt traps enhance the ir quenching efficiency. The recombination of holes at the cobalt traps may be radiationless or may produce an ir emission through an intermediate state as shown. It is to be noted in regard to the latter that Garlick has observed an ir fluorescence attributable to cobalt in a ZnS matrix.¹⁸

ACKNOWLEDGMENTS

The authors wish to express their thanks to A. Ferretti who prepared the phosphor samples and to E. Banks, W. Kiszénick, and N. Melamed for many helpful and stimulating discussions.

¹⁸ M. Dumbleton and G. Garlick, Proc. Phys. Soc. (London) B67, 442 (1954).