

Phosphorescence Mechanisms. IV. Decay Rate Spectra of Ruby, Uranium Glass, and Mn-Activated Zinc Sulfide

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(Received June 13, 1960)

Ruby, uranium glass, and a ZnS:Mn sample were studied by means of the phosphorometer in a program of measurement and analysis which included variation of temperature and average exciting intensity. It was not possible to identify any laws of temperature dependence, but there is strong evidence that part of the phosphorescence mechanisms operating in the ZnS:Mn sample involves recombination.

THE need for a high level of accuracy in the measurement of the phosphorogram has been stressed in the previous parts. The usual size of figure would serve as only a qualitative indication of data contained in the phosphorogram. Tabulation would require considerable space since almost all the phosphorograms discussed in the following are capable of analysis in the form of a decay rate spectrum, so the adopted course is to display only the concise and meaningful decay rate spectra and their respective rms differences. The phosphorograms themselves can be reconstructed very approximately by convoluting the components of the decay rate spectra with the elementary function (3) of Part III. An exception is made in the simple case of ruby.

RUBY

The specimen was a synthetic gem which had been rejected because of an imperfection in the cutting and polishing process. The gem was crushed and mounted as a powder. The concentration of Cr was 0.38% by weight. The experimental points of the phosphorograms of ruby at room temperature are shown in Fig. 1. It will be seen that at high frequencies the points approach a horizontal asymptote which is significantly above zero. This indicates the fraction of emitted energy which is converted by a process too fast for quantitative detection by the instrument ($\sim 60\,000\text{ sec}^{-1}$). The remainder

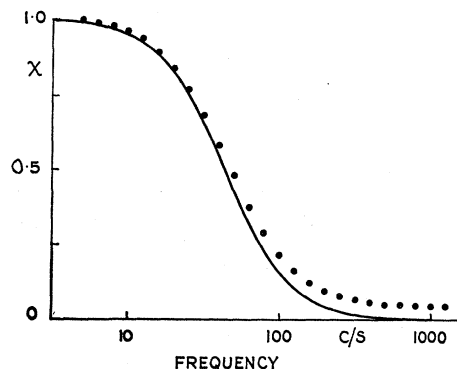


FIG. 1. Phosphorogram of ruby at room temperature. Circles represent experimental points. The full line is the theoretical phosphorogram for a single process mechanism at 278 sec^{-1} .

of the phosphorogram resembles the theoretical curve for a single component. However on closer examination it is found to be slightly asymmetric with the high-frequency side falling less steeply than the low-frequency side. The inference is that there is a component of much smaller weight with a rate constant somewhat higher than the main component. As an example the best solution with two processes is also included in the decay rate spectrum table (Table I). The full line in

TABLE I. Trial decay rate spectra of ruby.

No. of components	Weight	Rate (sec^{-1})	rms difference
2	0.955	290	0.0058
	0.045	$> 60\,000$	
3	0.915	278	0.0038
	0.040	790	
	0.045	$> 60\,000$	

Fig. 1 is the theoretical phosphorogram for a single component at 278 sec^{-1} .

Since the aim of the analysis is to reduce the rms difference to about 0.002, the figure for three components 0.0038 is still undesirably high even though it is a substantial reduction from the 2-component value. The fit is spoiled by the six points at the extreme low-frequency end which are consistently high compared with the theoretical curve. No other mechanism has been found to account for this satisfactorily, but since the deviation is small, it is probably best attributed to an unknown experimental maladjustment. The introduction of a further component does not effect any improvement to the fit, and should not be considered as a possibility. The decay rate spectrum is shown in Fig. 2.

The actual phosphoroscope measurements of Garlick and Wilkins¹ are available which illustrate the power of the present method. In Fig. 3 their experimental points are compared with the relation

$$I/I_0 = 0.915e^{-278t} + 0.040e^{-790t},$$

where the rate constants and weighting factors are taken

¹ G. F. J. Garlick and M. F. H. Wilkins, Proc. Roy. Soc. (London) **A184**, 408 (1945).

from the phosphorometer data in Table I. The curvature due to the second term is barely perceptible in a $\log I$ vs t representation. The original figure shows a slightly curved line through the points, but the present measurements suggest that from about 2 milliseconds onwards a straight line is to be preferred.

Recent "pulse taumeter" measurements of Tolstoi and Tkachuk² on ruby show the variation of the lumped rate constant with emission wavelength, temperature, and Cr content. It would appear that their technique is entirely complementary, and that where the results can be compared there is no discrepancy. In the relevant case the rate constants associated with all the emission wavelengths accepted by the phosphorometer cover a range $\Delta n = 2$. The present technique should resolve this as two distinct components in a favorable case, but here the much greater intensity of the doublet would make resolution impossible.

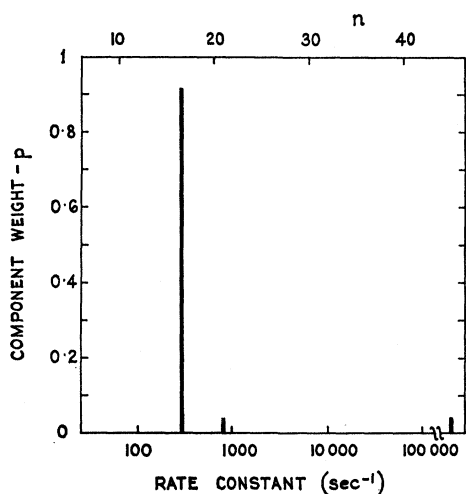


FIG. 2. Decay rate spectrum of ruby.

URANIUM GLASS

The sample of uranium glass was crushed to a powder like the ruby sample so that increased scattering of the incident energy would also increase its absorption and consequently the emission intensity. Phosphorograms were measured at liquid oxygen and ambient temperatures. Both were amenable to unambiguous analysis as a set of concurrent components. The rms difference was close to 0.002 in both analyses. The decay rate spectra are compared in Fig. 4. Despite considerable changes of component weight there is a clear correlation between the decay rate spectra at the two temperatures, although a small fast component beyond the range of the instrument appears only at the lower temperature.

Measurements at only two temperatures are insufficient to determine any law of rate constant variation,

² N. A. Tolstoi and A. M. Tkachuk, *Optika i Spektroskopiia* 6, 659 (1959) [translation: *Optics and Spectroscopy* 6, 427 (1959)].

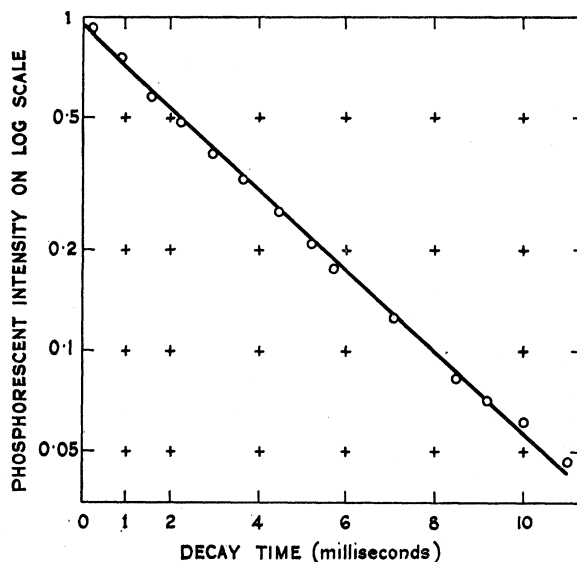


FIG. 3. Comparison with phosphoroscope technique. Circles represent the experimental points for ruby obtained by Garlick and Wilkins. The full line is computed from the decay rate spectrum.

but if the simple activation energy law

$$\alpha = s \exp(-E/kT)$$

is approximately obeyed, the activation energy E and the temperature-independent frequency factor s may be estimated. The result of this analysis is given in Table II which also incorporates calculations from much earlier work on this material. The shift of rate constant is given in logarithmic units,

$$n = 10 \log_{10}(\alpha/2\pi),$$

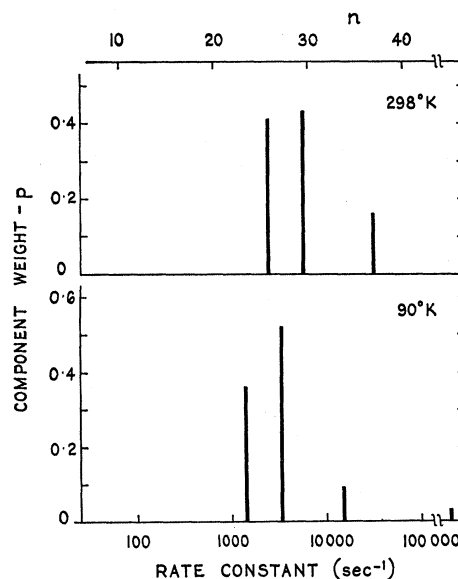


FIG. 4. Decay rate spectra of uranium glass at two different temperatures.

TABLE II. Analysis of uranium glass phosphorograms.

Temp. Component	90°K		298°K		Shift Δn (log units)	E (ev)	s (sec ⁻¹)
	Weight	Rate (sec ⁻¹)	Weight	Rate (sec ⁻¹)			
1	0.36	1410	0.41	2360	2.25	0.0058	2900
2	0.52	3300	0.43	5540	2.25	0.0058	6900
3	0.09	14 700	0.16	29 000	3.00	0.0077	40 000
4	0.03	>60 000	0
D & P ^a	1.00	3100	1.00	3400	0.4	0.001	3500

^a These data are derived from phosphoroscope measurements of R. Delorme and F. Perrin, J. phys. radium **10**, 177-186 (1929).

which were introduced in Part III. The equality of the logarithmic shifts of rate constant for the two major components is striking and may be the clue to a satisfactory account of the whole phosphorescence mechanism in this material. Since the error in the determination of the rate constants of the first two components can hardly be more than 0.05 (log units) the measurements of the shift should be accurate to about 5%. Thus the equality is unlikely to be fortuitous.

MANGANESE ACTIVATED ZINC SULFIDE

A small impure batch of ZnS was fired with about 4% MnS for investigation by the phosphorometer as a possible example of a bimolecular mechanism. The resulting phosphor was adequately efficient and its orange emission was characteristic of Mn activation. This material proved to be much more temperature sensitive than the two previously tested, and sufficient reproducibility of the phosphorograms was only obtained after constraining the sample temperature within a range of 1°C at ambient temperature. For this reason the first exploration concerned temperature dependence rather than intensity dependence of the decay rate spectrum. The phosphorograms were invariably less steep than those of the other two materials. Five components were found within the range of the phosphorometer, and energy was also distributed outside this range at either end. No comparable structure is found in the emission spectra, and it is not obvious how the peaked absorption spectrum qualitatively observed by Kröger³ could be

usefully correlated with the components of the decay rate spectrum.

Temperature Dependence

Table III gives the decay rate spectra for six temperatures of the sample all at the same average exciting intensity. The rate constants are given in logarithmic units, and the rms differences are given at the bottom of the table. In each case the analysis was over 37 points at intervals of one logarithmic unit of frequency ($\Delta m = 1$). The arrangement of Table III implies as with Table II the assumption that the components can in fact be correlated between one temperature and the next. Only measurements at intermediate temperatures could establish this definitely, and the additional labor was judged to be outside the scope of the present preliminary investigation. There appears to be no over-all temperature dependence of the decay rates apart from a rise at the higher end of the temperature range which is discussed in the next paragraph. However the detailed variations are in many instances more than ten times the experimental error, and cannot be discounted. Such variations could well have escaped previous detection with instruments of lower resolution.

Between 70° and 95°C there is a consistent rise of decay rate with temperature for each component (Nos. 2-6). Kröger³ made measurements of the efficiency of a possibly similar phosphor which showed it to begin to decline at these temperatures, and later⁴ in the case of

TABLE III. Comparison of analyses of ZnS:Mn phosphorograms at six different temperatures.

Component	Approx. rate (sec ⁻¹)	Weight, p						Rate, n^a					
		95°	70°	45°	26°	2°	-180°	95°	70°	45°	26°	2°	-180°C
1	<20	0.04	0.04	0.03	0.02	0.02	0.07			Too slow			
2	50	0.05	0.03	0.07	0.10	0.15	0.13	9.6	8.8	10.3	8.2	8.8	8.4
3	250	0.15	0.08	0.23	0.21	0.16	0.11	19.2	14.6	16.6	14.9	16.75	15.9
4	1100	0.68	0.64	0.45	0.42	0.46	0.26	24.85	22.55	22.55	22.25	23.25	22.6
5	3000	0.035	0.15	0.14	0.16	0.08	0.04	30.4	27.05	26.95	27.00	28.2	30.0
6	60 000	0.025	0.03	0.05	0.04	0.07	0	40.5	39.0	38.4	39.0	41.6	...
7	>100 000	0.02	0.02	0.03	0.05	0.06	0.39			Too fast			
rms difference ^b $\times 1000$		1.6	2.0	1.5	1.3	1.7	1.6						

^a The rate is given in logarithmic units, $n = 10 \log_{10}(\alpha/2\pi)$.

^b Analyses made over 37 points in each case.

³ F. A. Kröger, Physica **6**, 369 (1939).

⁴ F. A. Kröger *et al.*, Physica **14**, 81 (1948); **14**, 425 (1948); **15**, 557 (1949).

several other phosphors showed that a loss of efficiency at high temperatures could be correlated with a rise of decay rate. It was cogently argued that both effects were the result of a competing dissipative process which was strongly temperature dependent. The incidental measurements of efficiency in the present sample were too uncertain to establish any loss of efficiency. It must however be recognized that the application of such a hypothesis to this phosphor would necessitate a separate dissipative process associated with each component and all taking effect at much the same temperature.

The variation of the component weights is more pronounced than that of their decay rates. The general shift of the phosphorograms toward higher frequencies with increasing temperature is shown to be due to a shifting of weight in the direction of components of higher decay rate, rather than to an increase in the rate of the individual components. The opposite trend is evident for the very fast component, No. 7.

A further phosphorogram was measured at dry ice temperature. It proved intractable to analysis as a decay rate spectrum but included no minimum that would

TABLE IV. Analysis of ZnS:Mn phosphorogram at 95°C and exciting intensity one half that used for Table III results.^a

Component	Weight	Rate constant, n	Δn
1	0.04	< 5	...
2	0.06	8.2	-1.4
3	0.14	18.0	-1.2
4	0.675	24.70	-0.15
5	0.04	30.4	0
6	0.025	40.5	0
7	0.02	> 45	...

^a The rms difference is 0.0025.

indicate a simple cascaded pair. It is possible that it should be considered on the lines of the example given in Part I. With only a single set of data the development of a technique of numerical analysis is almost impossible, and no reliance could be placed on the result. However it was possible to determine the weights of the extreme components Nos. 1 and 7 as 0 and 0.25, respectively.

Bimolecular Mechanism

The phosphorograms of the two materials discussed previously showed no dependence upon average exciting intensity, but with the ZnS:Mn sample the dependence was immediately apparent and more attention had to be paid to the reproducibility of the level of average exciting intensity between different sets of measurements. The highest temperature (95°C) was chosen for detailed study of intensity dependence because the decay rate spectrum at this temperature included the component of largest weight, and was at the time thought to be the simplest. A phosphorogram was measured at half the average exciting intensity, with the results given in

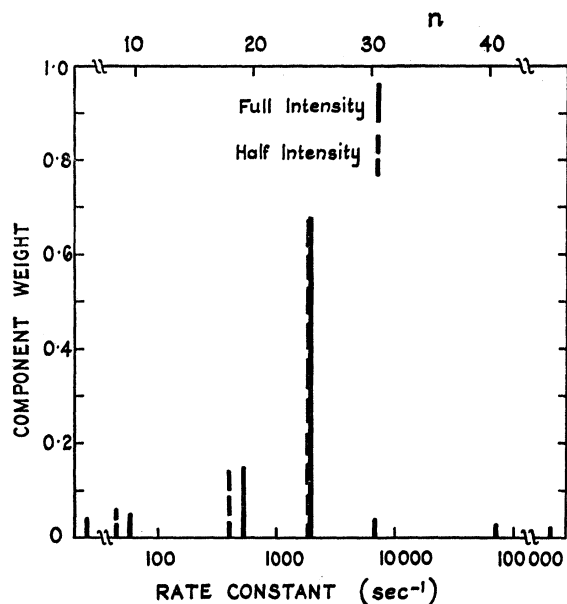


FIG. 5. Decay rate spectra of ZnS:Mn at 95°C with exciting intensity as parameter.

Table IV, and its decay rate spectrum is compared with that from the full intensity in Fig. 5. The rms difference, 0.0025, is significantly larger, but the individual differences are random. The increase may be due to the decreased signal:noise ratio at the lower intensity.

For a simple bimolecular component the predicted shift of rate constant for a halving of the average exciting intensity is $\Delta n = -1.5$. The shifts of components Nos. 2 and 3 are -1.4 and -1.2, respectively, which conform with this prediction to the first order. The theory (Part I) was based on the assumption that linearity is preserved between the measured intensity of excitation and the number of electrons per second raised to the appropriate upper state. The slight changes in the distribution of energy between the components suggest that linearity does not hold perfectly in the case of this sample. This may account for some of this discrepancy, but it is thought more probable that the crudeness of the theory is largely at fault. The shift of component No. 4 is too small for direct interpretation on this basis. It seems more likely that this largest component should be considered as the sum of two unresolved components of which the smaller is bimolecular and suffers a shift, and the larger is monomolecular and stationary. The ratio of their weights would have to be about 1:10, and the necessary separation would be comfortably less than the minimum separation resolvable by the phosphorometer.

GENERAL OBSERVATIONS

From our present state of knowledge it must be regarded as surprising that it has been possible to obtain

analyses in terms of *discrete* decay rate spectra. The resolution theorem of Part III shows that the "lines" could be somewhat broader, but the breadth could scarcely be comparable with the separation between the components.

Although only two materials have been examined at

low temperatures it is noteworthy that in either case the proportion of energy channelled through very fast phosphorescent processes is increased at low temperatures. At first sight this is hard to reconcile with the greater rigidity of selection rules to be expected at low temperatures.

Theory of Impurity Resistance in Metals*

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(Received June 27, 1960)

A many-body technique is developed for the calculation of the dc resistivity of a Fermi fluid in the presence of a few, randomly scattered, fixed, impurities. A certain class of graphs yields an expression for the conductivity which is similar in form to the standard classical transport coefficient; but the decay time is determined by the scattering of single-particle-like excitations at the Fermi surface by screened impurities. A propagator method similar to that used in field theory is employed throughout the paper, and the perturbation-theoretic interpretation of this method is examined in some detail.

I. INTRODUCTION

IN this paper we shall examine a many-particle formulation of the theory of impurity resistance in metals. The emphasis will be placed on an attempt to understand the role played by the electron-electron interactions. In order to do this most effectively, we shall adopt the simplest possible model which retains the essential features of interest in the physical system. In particular, we shall consider a dense Fermi gas of electrons moving in the presence of a uniform, positively charged, background and a few randomly scattered impurities. These impurities are fixed in the metal and are charged. Such a system is known to have a finite dc conductivity.

The present calculation will be further restricted in two ways. In the first place, we shall work only at zero temperature. Secondly, we shall consider only a relatively simple term in the conductivity which, as we shall see, yields a result similar in form to the standard classical expression for the transport coefficient. Our physical picture will be that of electrons accelerated by the external field and scattered by the impurities. Our "electrons," however, will turn out to be single-particle-like excitations of the Fermi fluid, and the impurities will be screened. It is hoped that the methods developed here will be useful in extending the calculation to finite temperatures and in estimating the higher order effects of electron correlations.

The first part of the development will be the derivation of a formal expression for the linear response of the system to a uniform electric field. The result, which is a special case of Kubo's formula,¹ has a simple interpretation in terms of many-particle graphs. It then will be

shown that the simplest class of these graphs leads to an expression for the conductivity very similar to the Greenwood-Peierls formula,² but generalized to include the many-electron effects mentioned above. This derivation is contained in Secs. II, III, and IV. Section V contains a discussion of the process of renormalization in many-body problems which is necessary for the interpretation of the results of Sec. IV.

The actual evaluation of the conductivity will be performed here using a method developed by Edwards.³ In Sec. VI the relevant features of Edwards' technique will be reviewed and generalized somewhat. In Secs. VII and VIII we shall make a detailed analysis of certain terms which appear and finally exhibit an explicit expression for the conductivity.

II. FORMAL EXPRESSION FOR THE CONDUCTIVITY

In order to calculate the conductivity, we take the system of electrons and impurities in its ground state Ψ_0 and slowly turn on a uniform electric field $\mathbf{E}(t)$. It is convenient to describe this field mathematically by the vector potential $\mathbf{A} = -(c/\alpha)e^{i\alpha t}\mathbf{E}$, which yields

$$\mathbf{E}(t) = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} = \mathbf{E}e^{i\alpha t}.$$

The conductivity σ then follows from examination of the current produced by \mathbf{E} at time $t=0$ in the limit $\alpha \rightarrow +0$.

To first order in \mathbf{E} , the state $\Psi(t=0)$ is given by

$$\Psi(0) = \Psi_0 - i \int_{-\infty}^0 dt e^{iHt} H'(t) e^{-iHt} \Psi_0 + \dots, \quad (2-1)$$

* Supported in part by the Office of Naval Research.

¹ R. Kubo, J. Phys. Soc. Japan 12, 570-586 (1957).

² D. A. Greenwood, Proc. Phys. Soc. (London) 71, 585 (1958).

³ S. F. Edwards, Phil. Mag. 3, 33, 1020 (1958).