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Mechanism of Impurity Poisoning in the Luminescence of Zinc Sulfide Phosphors with Manganese Activator

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An investigation was made of the poisoning effects of iron, cobalt, and nickel impurity in cub.-ZnS:Mn phosphors. The parameters varied included: (1) proportion of manganese, (2) proportion of poison impurity, (3) photon energy of the exciting radiation, (4) intensity of the exciting radiation, and (5) operating temperature of the phosphor. Analysis of the results shows that the two most important poisoning mechanisms are: (1) dissipation by poison centers of energy absorbed by the host crystal before this energy has been used to excite activator centers, a mechanism relatively independent of the proportion of manganese and type of poison, and (2) dissipative interaction between activator and poison centers, a mechanism which depends strongly on the proportion of manganese and type of poison. The first mechanism predominates when the primary excitation is absorbed by the host crystal, whereas the second predominates when the activator centers are excited directly.

INTRODUCTION

THE poisoning of phosphors by the incorporation of small traces of certain impurities has been known for some time.[1] One of the authors[2] has reported detectable poisoning of the cathodoluminescence emission of cub.-ZnS:Ag phosphor by iron, cobalt, and nickel for 0.0001 percent of these impurities. The poisoning of zinc orthosilicate with manganese activator by iron impurity has been investigated by Nagy and Bodo.[3] Some of the poisoning effects of iron, cobalt, and nickel impurity in ZnS:Cu have been described by Arpiarian and Curie.[4]

There are at least three possible, essentially different, mechanisms for the poisoning effect of such impurities. (1) The centers formed by the poison impurity may be able to dissipate the energy absorbed by the host crystal, before this energy is transported to activator centers. (2) The centers formed by the poison impurity may interact with activator centers. The nature of this interaction will be discussed together with the experimental results of this paper. (3) The centers formed by the poison impurity may absorb either the exciting radiation or the luminescence emission and convert the energy nonradiatively.

In order to determine the relative importance of these three possible mechanisms, it is helpful to be able to selectively excite (1) by absorption by the host crystal, and (2) by absorption by activator centers directly. Luminescence associated with excitation by host-crystal absorption (hereafter called *HC* excitation) may be poisoned by any or all of the mechanisms mentioned above; luminescence associated with direct activator excitation (hereafter called *A* excitation) may be poisoned by only the last two mechanisms.

It has been reported[5] that the emission associated with manganese activator in ZnS:Mn phosphors can be excited (1) by host-crystal absorption, if the excitation energy is greater than 3.3 ev; or (2) by direct activator excitation, if the excitation energy is between 2.2 and 3.3 ev (four activator excitation peaks for ZnS:Mn being located at 2.45, 2.60, 2.87, and 3.12 ev).

This paper presents the results of measurements of the excitation efficiency of cub.-ZnS:Mn phosphors, as a function of both manganese and of poison (Fe, Co, and Ni) proportion. The results show that all three possible poisoning mechanisms are effective, their relative importance depending on the activator and poison proportions, and on the energy of the exciting radiation. Poisoning found for *A* excitation is primarily associated with interaction between poison and activator centers. Poisoning found for *HC* excitation is primarily associated with the dissipation by poison centers of the host-crystal energy before it has been transported to activator centers. Poisoning effects due to absorption by poison centers are important only for high proportions of poison impurity.

EXPERIMENTAL

Preparation of Materials

The phosphors used in this investigation were prepared from triple-purified, spectroscopically pure ZnS (RCA LM476). The proper proportions of manganese chloride and the chloride of the poison impurity were added with 2 percent of sodium chloride[6] as solutions in triple-distilled water. The phosphor mixes were dried at 110°C, and heated at 800°C for 20 minutes in a stationary atmosphere of purified nitrogen.

The use of an atmosphere of purified nitrogen is necessary to obtain reproducible results of excitation

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[1] See, for example, H. W. Leverenz, *An Introduction to Luminescence of Solids* (John Wiley and Sons, Inc., New York, 1950), pp. 333–337.

[2] S. Larach, J. Chem. Phys. **18**, 896 (1950).

[3] E. Nagy and Z. Bodo, Acta Phys. Acad. Sci. Hung. **2**, 175 (1952).

[4] N. Arpiarian, Compt. rend. **233**, 387 (1951); N. Arpiarian and D. Curie, Compt. rend. **234**, 75 (1952).

[5] R. H. Bube, Phys. Rev. **90**, 70 (1953).

[6] All proportions are given in weight percent.

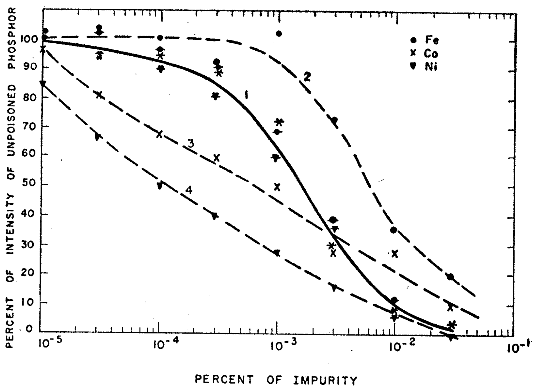

FIG. 1. The relative excitation efficiency of cub.-ZnS:Mn(1.0) phosphors as a function of various poison proportions. (1) Fe, Co, Ni impurity (experimental points with horizontal crossbar) for excitation by host-crystal absorption. (2) Fe impurity for activator excitation. (3) Co impurity for activator excitation. (4) Ni impurity for activator excitation.

efficiency for *A* excitation. The efficiency for *A* excitation is extremely sensitive to the presence of oxygen in the preparation atmosphere. Compared to a ZnS:Mn (1.0) phosphor prepared in purified nitrogen, a ZnS:Mn(1.0) phosphor prepared in an atmosphere of 88 percent nitrogen and 12 percent oxygen had 75 percent of the efficiency for *HC* excitation, but only 6 percent of the efficiency for *A* excitation. These results are similar to those previously reported,[5] which showed that the photoexcitation efficiency of ZnS:Mn phosphors, especially for radiation absorbed by the activator directly, is very dependent on whether the manganese is added as the chloride or the nitrate.

Measurements

The excitation source for the measurement of excitation spectra was a 500-mm Bausch and Lomb grating monochromator with incandescent light source. The emission of the phosphor was detected with a 1P21 phototube through a Corning 3480 filter. The photocurrent was passed through a Leeds and Northrup micromicroampere amplifier, and could be read directly or recorded on a Leeds and Northrup X-Y recorder.

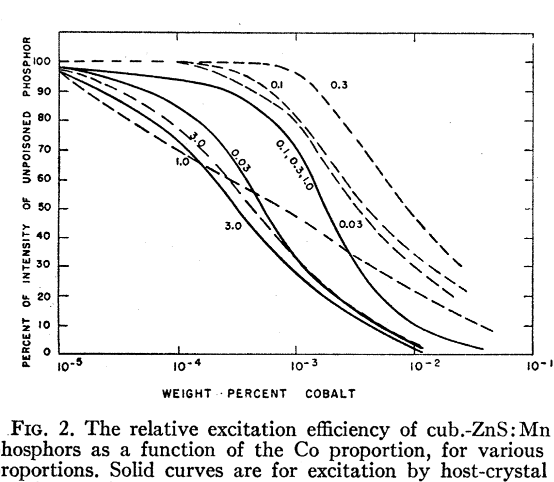

FIG. 2. The relative excitation efficiency of cub.-ZnS:Mn:Co phosphors as a function of the Co proportion, for various Mn proportions. Solid curves are for excitation by host-crystal absorption; dashed curves are for direct activator excitation. Numbers on the curves indicate the Mn proportion.

Measurements of diffuse reflectivity were obtained with a multiple reflection method previously described,[5] using a $MgCO_3$ integrating sphere, and detecting the reflected light with a recording grating spectroradiometer, to be described in a future publication.

Measurements of luminescence emission intensity as a function of operating temperature were made with the apparatus described in previous investigations.[7] The excitation source was an incandescent lamp with Corning 5860 filter for host-crystal excitation, and with Wratten 47 and Farrand 4730A filters for activator excitation.

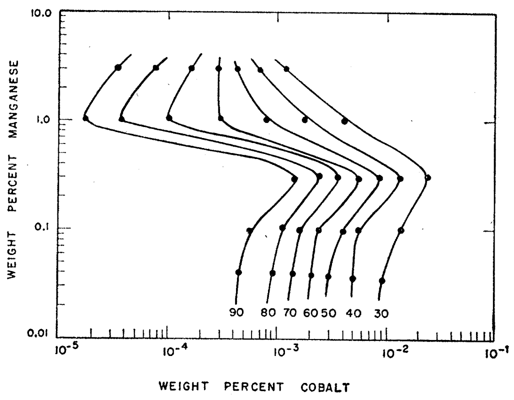

FIG. 3. Equal-poisoning contours for cub.-ZnS:Mn:Co phosphors as a function of Mn and Co proportions. The number below each curve is the percent of the intensity of the unpoisoned phosphor.

RESULTS

Excitation Efficiency as a Function of Mn and Poison Proportion

The data obtained from measurements of excitation efficiency are given in Figs. 1 through 5.[8] Figure 1 gives the relative excitation efficiency for cub.-ZnS:Mn(1.0) as a function of the proportion of Fe, Co, and Ni impurity. Experimental points are included in this figure to indicate the reliability of the data. Poisoning found for *HC* excitation is approximately the same for Fe, Co, and Ni; poisoning found for *A* excitation is markedly different for the different poisons.

Figure 2 gives the relative excitation efficiency for cub.-ZnS:Mn phosphors as a function of the proportion of Co, for proportions of Mn between 0.03 and 3 percent. Poisoning found for *HC* excitation is independent of the Mn proportion between 0.1 and 1.0 percent Mn; poisoning found for *A* excitation is markedly dependent on the Mn proportion over the same range. Figure 3

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[7] R. H. Bube, Phys. Rev. **80**, 655 (1950).

[8] For these figures, *HC* excitation is by 3.65-ev ultraviolet; *A* excitation is by 2.60-ev light.

is a replot of Fig. 2, showing lines of equal poisoning as a function of Mn and Co proportions.

Figures 4 and 5 are the results for Fe impurity, equivalent to Figs. 2 and 3 for Co impurity. Again it is found that poisoning for *HC* excitation is independent of Mn proportion between 0.1 and 1.0 percent, whereas poisoning for *A* excitation is very dependent on the Mn proportion over this same range. A comparison of the equal-poisoning plots of Figs. 3 and 5 shows a similarity of contour between them. Fair quantitative agreement on poisoning is obtained if the poisoning for a phosphor with x-percent Mn by y-percent Fe is compared with the poisoning for a phosphor with $3x$-percent Mn by $(y/6)$-percent Co.

As detailed measurements have not been made for Ni as for Fe and Co impurity, but poisoning caused by Ni seems similar to poisoning caused by Co.

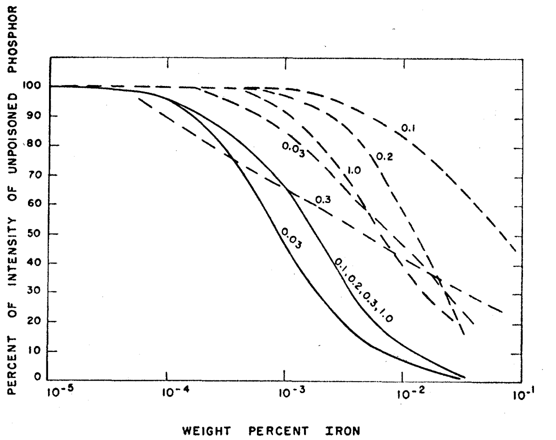

FIG. 4. The relative excitation efficiency of cub.-ZnS:Mn:Fe phosphors as a function of the Fe proportion, for various Mn proportions. Solid curves are for excitation by host-crystal absorption; dashed curves are for direct activator excitation. Numbers on the curves indicate the Mn proportion.

Reflectivity

Reflectivity spectra are given in Fig. 6 for phosphors without Mn and with 0.03 percent of each of the poison impurities, and for phosphors with 1.0-percent Mn and also 0.03 percent of each of the poison impurities. These spectra are compared with the reflectivity of a phosphor with 1.0-percent Mn only. It is found that (1) the absorption of phosphors containing Fe is very similar to that of phosphors containing Co, the absorption of phosphors with Fe or Co impurity being considerably less than for phosphors with Ni impurity; (2) the absorption by Fe or Co impurity in ZnS without Mn is small over most of the range of absorption by Mn centers; and (3) the absorption of ZnS:Mn phosphors in the range of absorption by Mn centers is increased by the incorporation of Fe, Co, or Ni.

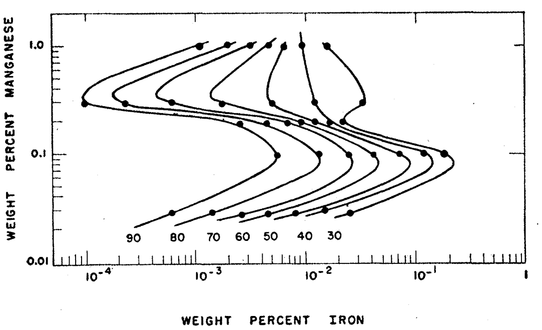

FIG. 5. Equal-poisoning contours for cub.-ZnS:Mn:Fe phosphors as a function of Mn and Fe proportions. The number below each curve is the percent of the intensity of the unpoisoned phosphor.

Poisoning as a Function of Excitation Energy

The data given in Figs. 1 through 5 for particular values of the excitation energy are equally valid for all other values of the excitation energy for the same type of excitation. If the exciting radiation has an energy less than about 2.9 ev, excitation is predominantly by activator absorption, and the variation of excitation efficiency with poison proportion is that found for *A* excitation. If the exciting radiation has an energy greater than about 3.2 ev, excitation is predominantly by host-crystal absorption, and the variation of excitation efficiency with poison proportion is that found for *HC* excitation.

The lack of dependence of excitation efficiency on excitation energy was checked particularly for cub.-ZnS:Mn(1.0):Ni phosphors since the absorption of these phosphors is a rapidly varying function of excitation energy in the range of Mn absorption. No

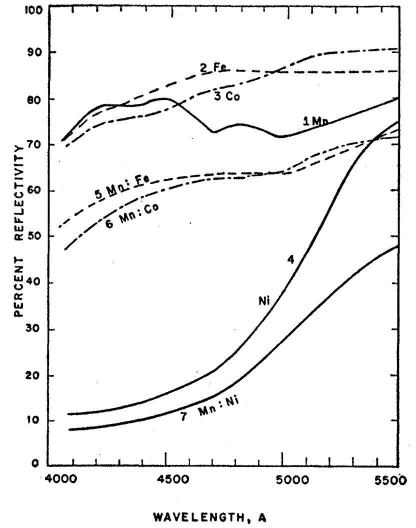

FIG. 6. Diffuse reflectivity spectra for cub.-ZnS phosphors with (1) 1.0 percent Mn; (2) 0.03 percent Fe; (3) 0.03 percent Co; (4) 0.03 percent Ni; (5) 1.0 percent Mn and 0.03 percent Fe; (6) 1.0 percent Mn and 0.03 percent Co; and (7) 1.0 percent Mn and 0.03 percent Ni.

difference in poisoning was found for excitation energies ranging from 2.25 to 2.7 ev (4600–5500A).

Poisoning and the Emission Spectrum

Because of the possibility that the emission spectrum of a ZnS:Mn phosphor might be altered if the poison impurity absorbed in the spectral region of the luminescence emission, emission spectra of cub.-ZnS: Mn(1.0):Ni(0.0003) (a phosphor with only 40 percent of the emission intensity of an unpoisoned cub.-ZnS: Mn(1.0) phosphor) were measured for excitation energies of 3.95 and 2.65 ev. (The path of the emission resulting from 2.65-ev excitation would be considerably longer in the material than the path of the emission excited by 3.95-ev ultraviolet.) No differences were found between the spectra of the emission obtained for this poisoned phosphor, which were the same as spectra obtained for an unpoisoned phosphor.

Emission Intensity as a Function of Excitation Intensity

In order to test the possible dependence of measurements of excitation efficiency on excitation intensity, measurements were made of the excitation efficiency of cub.-ZnS:Mn(0.3):Fe as a function of the Fe proportion for excitation intensities varying by a factor of fifty. The excitation intensity used for the data of Fig. 4 was intermediate in this range. No differences in poisoning were found, either for *HC* excitation or for *A* excitation.

As an additional check, the emission intensity of cub.-ZnS:Mn(1.0):Ni(0.001), cub.-ZnS:Mn(1.0):Co(0.003), cub.-ZnS:Mn(1.0):Fe(0.01), and cub.-ZnS:Mn(0.3): Co(0.01), were measured as a function of excitation intensity. A linear relationship between intensity and excitation intensity was found for excitation intensities varying by a factor of three thousand.

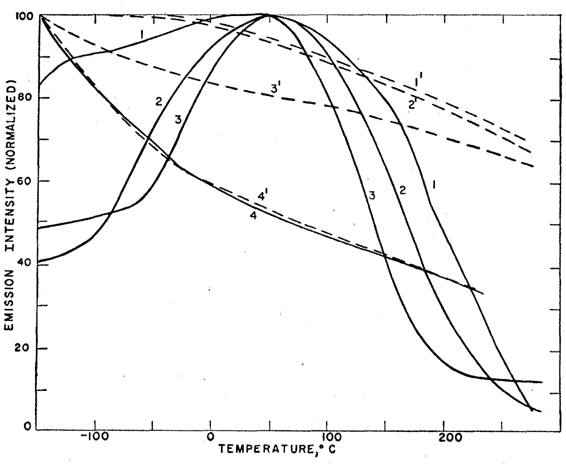

FIG. 7. Emission intensity of cub.-ZnS:Mn(1.0):Co phosphors as a function of operating temperature. Solid curves are for excitation by host-crystal absorption; dashed curves are for direct activator excitation. (1) and (1′) 0.00001 percent Co; (2) and (2′) 0.001 percent Co; (3) and (3′) 0.003 percent Co; (4) and (4′) 0.03 percent Co.

Emission Intensity as a Function of Temperature

Measurements of the emission intensity as a function of operating temperature were made for cub.-ZnS: Mn(1.0):Co phosphors for 0.00001, 0.001, 0.003, and 0.03 percent of Co, for both *HC* excitation and for *A* excitation. The data are given in Fig. 7. A marked difference in curve shape with type of excitation is found[5] for all but the most poisoned phosphor.

For *HC* excitation the emission intensity has a breakpoint at about 50°C. The location of this breakpoint does not change with poisoning at least until more than 70 percent of the unpoisoned phosphor's intensity has been lost; the rate of decrease of emission intensity with temperature past the breakpoint, however, increases with increased poisoning. (The variation of emission intensity with temperature below the breakpoint is probably due to the presence of traps and is characteristic of most sulfide phosphors.) When the phosphor has been severely poisoned, so that only 2 percent of the unpoisoned phosphor's intensity remains, the breakpoint lies below −150°C, and the variation of the emission intensity with temperature is identical for *HC* excitation and for *A* excitation.

For *A* excitation, a breakpoint of emission intensity is found at about −10°C for the unpoisoned phosphor, followed by a very slow decrease in intensity with increasing temperature. This breakpoint shifts to lower temperatures with increasing poisoning, lying below −150°C for phosphors which have lost 70 percent or more of the intensity of the unpoisoned phosphor.

DISCUSSION

Poisoning for Excitation by Host-Crystal Absorption

When excitation energy is absorbed by the host crystal, it must be transported by free electrons and holes, by excitons, or by some other mechanism, to activator centers before luminescence can occur. There are three principal points of the process at which the presence of poison centers can affect the luminescence efficiency: (1) the poison centers may interfere with the transport of energy to activator centers; (2) the poison centers may interact with activator centers to reduce or destroy their efficiency; and (3) poison centers may absorb the emission.

The data of Figs. 1, 2, and 4 show that poisoning for excitation by host-crystal absorption is independent of the Mn proportion between 0.1 and 1.0 percent, and of the particular poison used (Fe, Co, or Ni) over this same range of Mn proportion. These results indicate that both interaction and absorption by poison centers are relatively unimportant as poisoning mechanisms for *HC* excitation over a wide range of Mn proportions. Interaction between poison centers and activator centers would be a function of both the Mn proportion and the particular poison used. The absorption of ZnS:Mn phosphors with Fe or Co impurity is considerably less in the region of the emission spectrum than the absorption of ZnS:Mn phosphors with Ni impurity, and hence poisoning by Ni impurity absorption would be larger than poisoning by Fe or Co impurity absorption. It is concluded, therefore, that poisoning found for *HC* excitation is associated primarily with the dissipation by poison centers of host-crystal energy before the transport of this energy to activator centers may be accomplished.

For low proportions of Mn, such as 0.03 percent shown in Figs. 2 and 4, an increase in poisoning may be associated with the increased distance between activator centers. The average path, over which energy absorbed by the host crystal must be transported to activator centers to produce luminescence, becomes longer, and an increased probability of dissipation by poison centers is introduced.

For high proportions of Mn, such as 3.0 percent shown in Fig. 2, the variation of excitation efficiency with poison proportion is the same for *HC* excitation as for *A* excitation. For these high Mn proportions, the poisoning effect of interaction between poison centers and activator centers is more important than the poisoning caused by the dissipation of host-crystal energy before this energy has been transported the relatively short distances to activator centers. The dominating factor is the effect of interaction on activator centers, and poisoning is not affected by the nature of the excitation.

The curves of emission intensity as a function of phosphor temperature given in Fig. 7 for *HC* excitation show that the incorporation of a poison increases the probability of the dissipation of host-crystal energy by thermal processes above the temperature breakpoint. When the phosphor is severely poisoned, it becomes improbable for host-crystal energy at any temperature where measurements were made to be transported over any appreciable distance in the crystal, and it is only the host-crystal energy which is absorbed in the immediate neighborhood of an activator center which may be utilized. The temperature variation of the emission intensity is then dependent upon the temperature variation of the efficiency of the activator center, as affected by interaction; curves of emission intensity *vs* temperature are the same for *HC* excitation as for *A* excitation (Fig. 7, curve 4). The beginning of this condition in less poisoned phosphors may be observed by comparing the variation of emission intensity at high temperatures for curves 1, 2, and 3 of Fig. 7. In these less poisoned phosphors, the dissipation of host-crystal energy at high temperatures is so large that once again the emission intensity for *HC* excitation varies with temperature in the same way as the emission intensity for *A* excitation.

Poisoning for Direct Activator Excitation

When the Mn activator centers are excited directly, electrons are raised to excited states of the Mn ions, but remain bound in the neighborhood of their parent ions. Poisoning by the incorporation of impurities may enter in three principal ways: (1) the poison centers may absorb the exciting radiation and thus decrease the density of excitation for activator centers; (2) the poison centers may interact with activator centers to reduce or destroy their efficiency; and (3) the poison centers may absorb the emission.

The fact that the absorption characteristics of Fe and Co impurities are similar to one another, but quite different from those of Ni impurity, whereas poisoning caused by Fe is quite different from that caused by Co or Ni, indicates that absorption effects play only a minor role in poisoning unless the poison impurities are present in very high proportions.

The dependence of poisoning for *A* excitation upon the proportion of Mn and the particular poison used indicates that an interaction between poison centers and activator centers is the principal poisoning mechanism.

Except for establishing the similarity between the complicated poisoning characteristics of Fe and Co impurity, the results of the present study have not led to date to an adequate explanation of the variation of poisoning with Mn proportion. For each poison impurity, all curves of excitation efficiency as a function of increasing log poison proportion show a relatively rapid decrease after some poison proportion, except for one proportion of Mn (1.0 percent Mn for Co and Ni, 0.3 percent Mn for Fe). For this critical proportion of Mn, which is also the proportion for which maximum poisoning is obtained for low poison proportions, the excitation efficiency is almost a linearly decreasing function of the log poison proportion.

The data, however, do allow conclusions to be drawn about the nature of the interaction between poison centers and activator centers. The interaction must (1) decrease the efficiency of an activator center by either affecting nonradiative processes within the center, or by dissipating the energy through a transfer from activator to poison center; (2) increase the absorption of radiation in the range of the Mn absorption by poisoned activator centers; and (3) prevent a poisoned activator center from being excited by acquisition of energy from the host crystal. The last effect of the interaction is indicated by the fact that a lower excitation efficiency may be found for *A* excitation than for *HC* excitation for the same impurity proportion. The increased absorption of incident radiation by poisoned activator centers would also play a part in producing this observed effect.