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The central aim of the research accomplished under this contract has been an increased understanding of the processes of optical excitation and energy transfer in insulators and semiconductors, based on experimental studies of absorption, luminescence, photoconductivity, and photo-emission. Emphasis has been placed on those phenomena which are properties of the pure material, or of the simpler kinds of lattice imperfections. This report summarizes the work done along these lines at the Institute of Optics during the past three years with the support of AFOSR. Much of this work has already been reported via the channels of Technical Notes and publications in the scientific literature. A list of these publications and an abstract of each appears in Appendix I. Reference (5)* contains a summary of progress in earlier work.

Only a brief comment on these researches will be made in this report. A more detailed description will be given of work which has not yet been published as well as that work presently in progress.

*The numerals in parentheses refer to the numbered references in Appendix I.

Previously Reported Work

Earlier work at the University of Rochester on the luminescence of the pure alkali halides has been continued and extended to include host-sensitized luminescence. The measurements of Teegarden (1) and Teegarden and Weeks (2) in the emission and excitation spectra of "pure" and thallium doped KI as a function of temperature have illuminated some of the mechanisms responsible for luminescence in the alkali halides. These experiments indicated that the recombination of free electrons with trapped holes plays an important part in the luminescence of pure, single crystal KI, and that the same mechanism may contribute in an important way to the excitation of room temperature luminescence in thallium doped KI. It was suggested by Teegarden (1) that the recombination of an electron with a hole trapped near an impurity center could cause excitation and subsequent luminescence of the impurity. This process, rather than excitons, for example, may be important in host-sensitized luminescence of the KI:Tl system.

A very considerable effort was made in an attempt to detect intrinsic photoconductivity in the alkali halides. In 1959, Teegarden (3) observed the onset of photoconductivity in single crystals of KI and RbI at room temperature and 203°K. This result is in contradiction to recent work reported from Cornell in which photoconductivity was not observed. In Teegarden's experiments, the threshold occurred at a wavelength somewhat shorter than the position of the first fundamental band in both materials and corresponded to the step on the high energy side of this band which had been tentatively associated with band-to-band transitions. The interpretation of the results was made extremely difficult by the possibility of photoemission from the surfaces of the crystals. Subsequent experiments by Nakai and Teegarden (9) have paid particular attention to this problem with the result that the separation of the photoconducting and photoemitting contribution to the observed photocurrents has been accomplished with reasonable certainty. The conclusion is that intrinsic photoconductivity has been observed in these materials with the threshold occurring at a wavelength corresponding to band-to-band transitions.

Tutihasi (4) has studied the optical absorption of the thallous halides in the ultraviolet as a function of temperature. He found interesting epitaxial effects in the shape of the absorption curve when TlCl films were formed by evaporation on a substrate (KCl) with the NaCl structure at low temperatures. By forming the films on KCl substrates at -180°C, the TlCl was forced into the NaCl structure, which normally is the stable modification only for high temperature.

Under these conditions, the first exciton peak was absent. After annealing, TlCl transforms into the CsCl structure, the stable modification at low temperatures, and the first exciton band appeared. This indicated that this band is characteristic of the CsCl structure. Tutihasi also observed that the absorption curves for TlCl at low and high temperatures, crossed at an absorption coefficient of $\sim 3 \times 10^3$ cm^{-1}. As the temperature was lowered, the absorption peak moved to lower energy with a simultaneous increase in the slope of the low energy tail. At high temperatures, the slope of the tail decreased and the peak shifted to higher energies. This anomalous behavior is not observed with the alkali halides.

A considerable effort has gone into an extension of the previous work of Dutton and co-workers on the photoconduction properties of PbS. This work has not yet been completely reported and will be described briefly in the next section. However, there has been issued a technical note and publication by Smith (6) concerning a reflectometer developed for the vacuum ultraviolet in connection with this work. This instrument has found wide application in the research at this institution.

Unreported Work

At the close of this contract period, three research programs were being actively persued:

1) Dr. Dutton and his graduate student, Mr. A. Smith, have been investigating the photoelectric properties of PbS in the vacuum ultraviolet region of the spectrum (7). This work has recently been reported in a doctoral dissertation by Mr. A. Smith (8) and portions of this thesis will be published in the scientific literature (8,9,10) in the near future.

A majority of past investigators of the compound, lead sulfide, have devoted their attentions to its optical and electrical properties in the near infrared and visible wavelength regions. In recent years, however, techniques of ultraviolet and vacuum ultraviolet radiometry have been introduced and developed as a result of the increasing interest in optical and photoelectrical measurements on substances in this wavelength region. In the present work, measurements have been carried out on PbS in the wavelength range 850 Å to 3000 Å.

A detailed description of the instrumentation necessary for optical measurements in this range is presented in reference (8). Photoconductivity in chemically deposited layers of lead sulfide was investigated in the 1600 Å to 3000 Å range. At the higher energies, photoemission from PbS represent an important contribution to the observed currents, and therefore photoemission was measured in natural crystals of galena (in the 850 Å to 2500 Å range). The results of these investigations reveal that this well-known infrared photoconductor is also an extremely efficient photoemitter at short wavelengths. A consideration of the energy distribution of the emitted photoelectrons indicated that measurements of photoemission may often give insight into fundamental electronic processes in lead sulfide.

2) Preliminary data on the optical absorption in solid rare gases have been obtained by Dr. Baldini using krypton. Two strong absorption bands were observed at 1139 Å and 1216 Å at about 4°K, which are slightly displaced from the corresponding atomic emission doublet. The widths of the two bands are of the order of 0.1 ev and they fall at higher energy (about 0.2 ev) as compared with the atomic lines. Besides these two bands there appears to be a continuum with smaller and broader absorption bumps at 1005 and 1077 Å.

The experimental equipment consists of a Hanovia H_2 discharge lamp, grating monochromator, cryostat for liquid helium, photomultiplier, electrometer and recorder. The U.V. radiation was converted into visible light by means of 2, 2' - dihydroxy - 1, 1' napthaldazine (known in Russian literature as Liumogen) phosphor and collected by a 6199 RCA photomultiplier.

Pure krypton was deposited on one end of a sapphire cylinder kept in thermal contact with the helium reservoir of the cryostat; both ends had been previously coated with Liumogen. By rotating the helium container in the cryostat through 180° a measure of the incident and transmitted flux was obtained. Any absorption due the Liumogen and included impurities were calibrated out by measuring the transmission of the coated sapphire rod without the krypton film. Both Liumogen and solid krypton are transparent to the luminescent radiation, so that the relative transmission of the krypton film was determined from the ratio

$\frac{Lo}{L}$, where Lo is the luminescence of the phosphor due to the U.V. on the krypton free side of the sapphire cylinder and L is the luminescence of the U.V. transmitted by the krypton film. The absolute transmission was obtained by correcting the relative values for differences in the two Liumogen layers which was obtained in the calibration. There are no windows at the entrance slits and exit slits of the monochromator; liquid nitrogen traps condense the oil and water vapors present in the system.

Absorption spectra of Argon and Xenon are in progress.

Dr. P. Baumeister has initiated a program to study luminescence in the alkali halides, using specially purified materials. To this end, an apparatus has been constructed for zone refining crystals of the alkali halides in vacuo. The molten zone is to be produced by heating a graphite tube by electron bombardment, the empty tube having been first purified by heating to high temperature. A charge of alkali halide crystals is then to be added to the tube without breaking vacuum and zone purification begun. The vacuum tank for this process has been built and leak tested.

Prior to the initiation of this program, Dr. Baumeister completed some research on the optical absorption of cuprous oxide. This work had been begun and, to a large extent, completed before he joined the Institute of Optics.

Appendix I

Abstracts and References
to
Publications and Technical Notes

1. K. Teegarden, Technical Note AFOSR TN-58-917,
   Astia Document AD 204 563, November 1958.
   "Host Sensitized Luminescence in KI:Tl"

   Abstract - Host sensitized luminescence has been observed in a single crystal of KI doped with about one part in 10^5 of thallium. The quantum efficiency of the thallium luminescence stimulated at room temperature by irradiation in the fundamental bands of KI was about 0.1. At $93^{o}K$ the thallium luminescence is masked by the previously reported luminescence of undoped KI. Excitation and emission spectra for the room-temperature luminescence are given.

2. K. Teegarden and R. Weeks, J. Phys. Chem. Solids 10, 211-216 (1959); Technical Note AFOSR-TN-58-918, Astia Document AD 204 562, November 1958.
   "Trapped Charge and the Low Temperature Luminescence of Undoped KI"

   Abstract - New data are presented on the previously reported low-temperature blue luminescence of undoped KI. It is shown that the emission previously observed during irradiation in the fundamental bands can also be stimulated by irradiation in the F- and F' -bands formed

by exposure to ultraviolet light at 93°K. The crystals display a burst of red luminescence when warmed after irradiation with light absorbed in the fundamental bands at 93°K. No emission upon irradiation in the F-band occurs if the F-centers have been formed at room temperature. It is suggested that the red luminescence occurs when holes are released from traps during warming and that the blue luminescence is due to the recombination of electrons with trapped holes at 93°K.

3. K. Teegarden, Technical Note TN-59-303,
Astia Document AD-213087, April 1959.
"Photoconductivity in KI and RbI"
Abstract - A threshold for photoconductivity has been observed in single crystals of KI at room temperature and RbI at room temperature and 203°K. This threshold occurs at a wavelength somewhat shorter than the position of the first fundamental band in both materials and is presumed to result from band to band transitions. No photocurrent is observed in the region of the first fundamental band in either KI or RbI.

4. S. Tutihasi, J. Phys. Chem. Solids 12, 344-348 (1960);
Technical Note AFOSR TN-59-753, July 1959
"Ultraviolet Absorption in Thallous Halides"
Abstract - The ultraviolet absorption in TlCl and TlBr has been measured on thin films and fused samples as a function of temperature. The effect of excessive chlorine or thallium on the optical absorption of TlCl has been

studied. The experiments of Vysochanskii are discussed in the light of our observations.

The first absorption band in TlCl, which peaks at 3.44 ev at -185°C, is absent in films condensed on a cold substrate of KCl and appears after annealing. It seems that the crystal structure of evaporated films of TlCl changes from the NaCl-type to the CsCl-type.

5. D. L. Dexter, J. Phys. Chem. Solids 8, 473-481 (1959)

"Optical Investigations of Semiconductors at the University of Rochester"

Abstract - A survey is given of recent investigations at this institution of optical properties of nonmetals. The fundamental absorption of the alkali, silver, and thallous halides and of cadmium sulfide; intrinsic photoconducitvity in the alkali halides; electron multiplication in lead sulfide and selenide; and the theory of excitons in the tight binding approximation are among the topics discussed.

6. A. Smith, J. Opt. Soc. Am. 50, 862-864 (1960)

Technical Note. TN-

Astia Document AD-

February 1960.

"A Reflectometer for the Vacuum Ultraviolet"

Abstract - A newly designed device for the measurement of absolute reflectance in the vacuum ultraviolet region is discussed. Notable features of this reflectometer are compactness and simplicity. The source and monochromator with which the reflectometer is used are also discussed. The system produces data in the wavelength range 800 A to 2500 A at any angle of incidence between 15^{o} and 80^{o}. A sample reflectance curve for a crystal of KCl is shown.

7. A. Smith and D. Dutton, Paper Presented to Cornell Conference on Photoconductivity, August 1961; J. Phys. Chem. Solids (To appear) "Photoconductivity and the External Photoelectric Effect in PbS"

Abstract - We have measured the yields for photoconductivity and external photoemission in the vacuum ultraviolet spectral region, 584-3000 A, using polycrystalline layers and natural crystals. The photoconductive yield in PbS layers rises approximately linearly with incident photon energy hv up to 7.5 ev; further extension of the measurement was thwarted by the magnitude of the external photocurrent. The rise in yield, as previously reported by us, is attributed to collision multiplication beginning at hv_t - 2 ev. The observed photoelectric threshold for galena crystals was 5 ev, and for layers 6 ev. Both kinds of specimen exhibit very large external photoyields at high hv; 10 to 20 per cent at hv-14.5 ev. The energy distribution of emitted electrons was examined using retarding-potential methods. The high photoelectric thresholds imply that any electron with sufficient energy to escape would be subject to scattering due to collision multiplication, an effect expected normally to limit the attainable photoelectric yield. From the high ultimate yields that were observed, and from the changes in the energy distribution of the emerging electrons with increasing hv, we infer that scattering by collision multiplication, considered as a function of hv, is not a monotonically rising function, but has a maximum. The data suggest strongly that this occurs for incident photon energies of slightly more than 9 ev.

3. A. Smith, Ph.D. dissertation, University of Rochester (1961)
"Investigations of Photoconductivity and Photoemission In Lead Sulfide in the Vacuum Ultraviolet"

Abstract - A majority of past investigators of the compound, lead sulfide, have devoted their attentions to its optical and electrical properties in the near infrared and visible wavelength regions. In recent years, however, techniques of ultraviolet and vacuum ultraviolet radiometry have been introduced and developed so that there has been an increasing interest in optical and photoelectrical measurements on many substances in the shorter wavelength region. Such is the case for lead sulfide - the measurements that are discussed in this work involve the wavelength range 850 A to 3000 A.

A detailed description of the instrumentation necessary for optical measurements in this range is presented in the text prior to the experimental discussions. Photoconductivity in chemically deposited layers of lead sulfide is then considered (in the 1600 A to 3000 A range), and finally photoemission in PbS layers and in natural crystals of galena is considered (in the 850 A to 2500 A range). The results of these investigations reveal that this well known infrared photoconductor is also an extremely efficient photoemitter at short wavelengths. An important conclusion from this work is that measurements of photoemission may often give more insight into certain fundamental electronic processes in lead sulfide than can be obtained from investigations of photoconductivity.

9. A. Smith and D. Dutton, Phys. Rev. (to be published)

10. A. Smith and D. Dutton, J. Opt. Soc. Am. (to be published)

11. Y. Nakai and K. Teegarden, Paper presented to Cornell Conference on Photoconductivity, (1961); J. Phys. Chem. Solids (to appear).
"Photoconductivity in RbI and KI"

Abstract - A threshold for intrinsic photoconductivity has been observed in RbI and KI at room temperature and lower temperatures. These experiments were carried out

with an electrode arrangement quite different from that employed previously by Teegarden and in a considerably cleaner vacuum. Photoconductivity occurs on the short wavelength side of the first exciton band in the region of the shoulder previously ascribed to the onset of band to band transitions. Photoconductivity also can occur on the long wavelength side of the first exciton peak when F-centers or other kinds of electron surplus centers, formed by irradiation with ultraviolet light, are present in the crystals.

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