

Afterglow of Magnesium Oxide Single Crystals

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* Magnesium oxide single crystals have been irradiated with ultraviolet light at room temperature and the glow curves and accompanying electric current recorded simultaneously from room temperature to 300°C. The measurements of optical absorption show the disappearance of absorption bands in visible region. Trap depths of the luminescent centers are given.

I. INTRODUCTION

MAGNESIUM oxide is a useful material for studying electronic processes in divalent ionic crystals, since it has the advantages of being available in large single crystals, of being very inert, and, moreover, of having a simple body-centered cubic lattice with good cleavage. The fundamental properties of magnesium oxide are well known,¹ but its photoconducting properties are not sufficiently understood at present, because of its high resistivity. In recent years the measurements of its optical absorptions, produced by irradiation with ultraviolet light,² x-rays,³ and by coloring with magnesium and oxygen,⁴ have been performed. Also measurements of the photoconductivity associated with optical absorption have been recently carried out.⁵

In the present work the afterglow and accompanying electric current of single uncolored and colored crystals are measured in order to study the electronic processes in magnesium oxide. The disappearance of absorption bands associated with luminescence will be mentioned briefly.

II. EXPERIMENTAL PROCEDURE

Most of samples were cleaved on the order of one-half millimeter thick and one-half centimeter square from large clear (uncolored) single crystals supplied by the Norton Company.⁶ To study the effects of additive coloring, samples were colored with magnesium by heating them in magnesium vapor in a vessel of stainless steel at temperatures of about 1250°C to 1300°C for one hour (magnesium colored) and colored with oxygen by heating them in a stream of dry oxygen at temperatures of about 1300°C for two hours at a pressure of about one atmosphere (oxygen colored). Spectroscopic analysis revealed no impurities other than calcium (smaller than 0.1 percent). Conducting coatings of gold were sputtered on both sides of the plates.

The light emitted was received by a 1P21 R.C.A. photomultiplier tube followed by two Horton type dc amplifiers⁷ and a recorder. A cesium-silver oxide photo-

cell, with a 10^{11} ohm resistor, a UX-54 electrometer tube, and a dc amplifier, was also used because of its high sensitivity for the bitter orange luminescent light. In order to analyze the wavelength distribution of the light emitted, a Corning 3-68 filter which transmits light above 5600Å was interposed. The electrical current associated with luminescence was measured simultaneously with a 10^{11} ohm resistor and electrometer tube followed by a dc amplifier and recorder. Space-charge effects might be negligible because of the small current. The samples were warmed up at a constant rate of 5°C per minute which was so slow that a good resolution was obtained, except for temperatures below 35°C. The luminescent light entered a electrically shielded box containing the photomultiplier through a window of fused quartz on the top of the box. The temperatures were measured with chromel-alumel thermocouple which was in contact with the sample. The block diagram of the apparatus is shown in Fig. 1.

The plates were colored by irradiation with x-rays (50-kv, 10-ma, tungsten target) and unmonochromized mercury discharge light at room temperature. Both sources, however, gave the same glow and conduction curves in the temperature range studied, so that the latter was used mainly because of convenience. Saturation of coloration was obtained in about half an hour. Both glow and conduction curves obtained were reproducible.

III. RESULTS

(a) Afterglow and Accompanying Charge Conduction

The data for uncolored crystal are shown in Fig. 2. The solid curves of lower and higher intensity are the

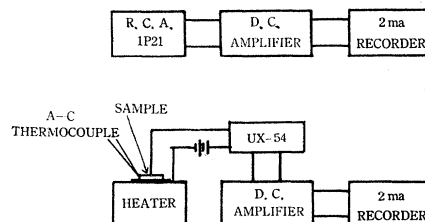


FIG. 1. Block diagram of the apparatus.

¹ See for example, F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

² J. H. Hibben, *Phys. Rev.* **51**, 530 (1937).

³ J. P. Molnar and C. D. Hartman, *Phys. Rev.* **91**, 1015 (1950).

⁴ H. Weber, *Z. Physik* **130**, 392 (1951).

⁵ H. R. Day, *Phys. Rev.* **91**, 822 (1953).

⁶ The Norton Company, Niagara Falls, New York. Appreciation is expressed to the Norton Company for making this work possible.

⁷ J. W. Horton, *J. Franklin Inst.* **216**, 749 (1933).

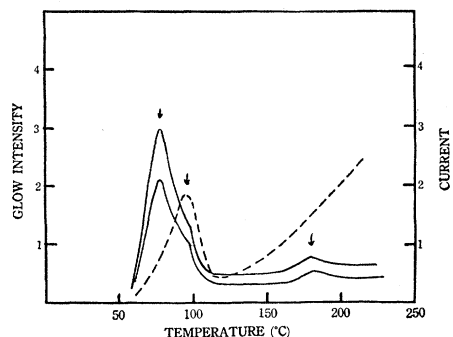


FIG. 2. Glow curves and conduction curve for uncolored crystal. The solid curve of lower and higher intensity are the glow curves obtained with and without a Corning 3-68 filter, which transmits light above 5600 Å, interposed between the crystal and phototube. The dotted curve shows the conduction current recorded simultaneously.

glow curves obtained with and without the Corning filter interposed. The shape of the curves is not altered by transmission through the filter, but the intensity is decreased about one-quarter. The dotted curve shows the conduction current. It is seen that the second peak of the glow curve (95°C) is accompanied by a peak in the electric current, but the first (77°C) and third (180°C) peaks are not. The gradual rise in the conduction curve might be caused by the current from an impurity level, as described later.

The glow and conduction curves for magnesium colored crystals, shown in Fig. 3, are almost the same of those for uncolored crystals below 150°C, except a small hump (65°C) in the glow curve of magnesium-colored crystals. However, there is no peak at 180°C in the glow curve, but a peak at 20°C, accompanied with large conduction current.

Finally the glow and conduction curves of oxygen colored crystals, shown in Fig. 4, are different from those of uncolored ones, since the peak at 95°C disappears in the glow and conduction curves, and the peak at 180°C in the glow curve becomes large. The various peaks in the glow and conduction curves are summarized in Table I.

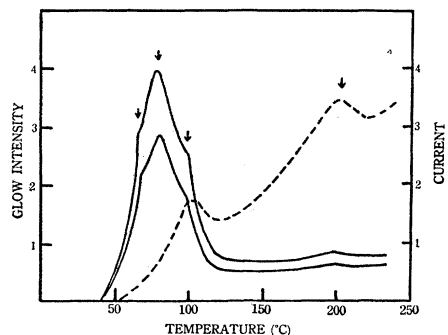


FIG. 3. Glow and conduction curves for the magnesium-colored crystal.

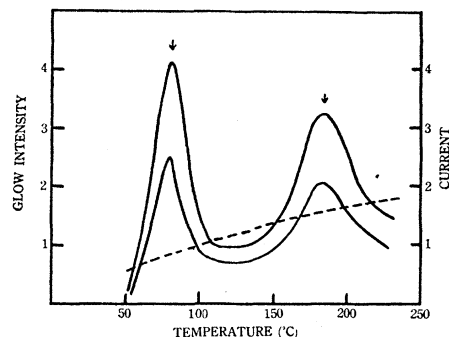


FIG. 4. Glow and conduction curves for the oxygen-colored crystal.

(b) Conductivity of Uncolored Crystals

The gradually increasing background in the conduction curve in Figs. 2, 3, and 4 was also found without irradiation with ultraviolet light. Measurements of conductivity against temperature were carried out in order to study its origin. A plot of current vs $1000/T$ (°K) for the uncolored crystal, measured with a UX-54 electrometer tube, has a slope of 2.1 eV in the higher-temperature range and of 0.58 eV in the lower-temperature range as shown in Fig. 5. The background in the conduction curve may be attributed to carriers originating from an impurity level which has the value 1.16 eV for the activation energy.

(c) Disappearance of Absorption Bands

Disappearance of the absorption bands associated with luminescence was measured by the following manner. The absorption of the irradiated crystal was measured, first at room temperature, and again at

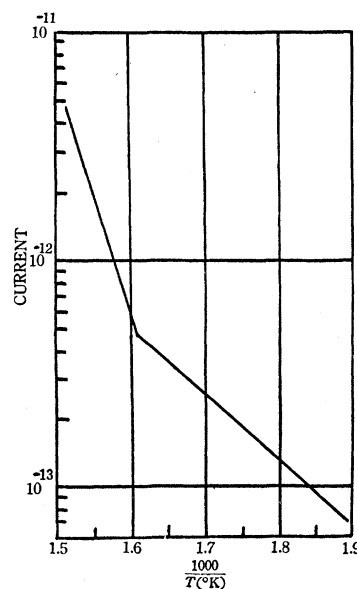


FIG. 5. Current vs $1000/T$ for the uncolored crystal.

room temperature after the crystal had been warmed momentarily to some higher temperature which corresponded with a peak in the glow curve. A succession of such measurements was made at temperatures corresponding to the various peaks after a definite duration of irradiation. The absorption curves of uncolored and colored samples without irradiation are shown in Fig. 6. It is seen that the uncolored clear samples show appreciable absorption in the ultraviolet range before coloring with oxygen and also that the magnesium-colored samples show slight absorption in that range. The additional absorption produced by irradiation with ultraviolet light in all samples occurred in the visible region without remarkable peaks. Momentary warming to about 100°C mainly decreased the band at 5200 Å which was produced by additive coloring with magnesium, as shown in Fig. 7, but the differences of variation of absorption bands between the samples of three types and the correspondence with various peaks in the glow and conduction curves could not be deduced

TABLE I. Summary of various peaks in the glow and conduction curves.

temp. °C of peaks		65	77	95	180	200
trap depth (ev)	$s = 10^8$	0.56	0.59	0.62	0.77	0.88
	$s = 10^{10}$	0.82	0.85	0.90	1.12	1.17
	$s = 10^{12}$	0.95	0.99	1.04	1.29	1.35
uncolored	glow		○	○	○	
	cond.			○		
magnesium-colored	glow	○	○	○		○
	cond.			○		○
oxygen-colored	glow		○		○	
	cond.					

because of the broad absorption band in the visible region.

IV. DISCUSSION OF RESULTS

The energies required for electrons or holes to move from their traps to luminescent centers are related to the temperatures at which the peaks of the glow curves occur. Trap depths E for the peaks are computed by the following formula from Randall and Wilkins:⁸

$$E = kT \log S \{1 + \log(kT^2/\beta E)/\log S\},$$

where β is the constant warming rate. Unfortunately the frequency S , the "attempt-to-escape" frequency, is not known accurately and, moreover, we could not estimate it from an experiment like that of Randall and Wilkins, because various curves were superimposed and could not be separated by the filter. If we assume that S is 10^6 , 10^{10} and 10^{12} sec⁻¹, the values in Table I are obtained.

⁸ J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) **A184**, 366 (1945).

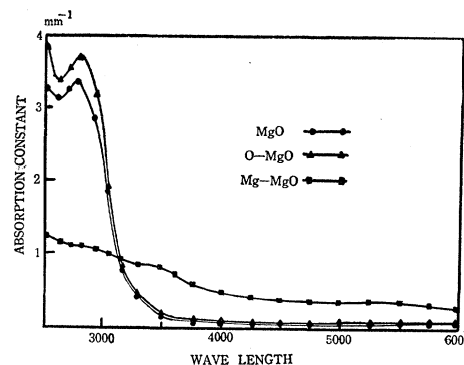


FIG. 6. Absorption curves for the uncolored, magnesium-, and oxygen-colored crystal. No correction for surface reflection is made.

Trap depths of the peaks in the glow curves that corresponded to peaks in the conduction curves represent the energy of a level below the conduction band that yields an electron to the conduction band, or a level above the filled band that yields a hole to the filled band. However, the derivation of the electronic model of the luminescent processes from this simple assumption seems to be hasty. Day⁵ has concluded from his measurements of photoconductivity that the photocurrent associated with the absorption bands which appear in magnesium-colored crystal was carried by holes. Furthermore he concluded that these optical transitions measure the energy of the localized levels above the filled band. This view seems to be different from that usually accepted. On the other hand, it is possible that the localized level in a divalent crystal which contains excess positive ions is so far below the conduction band that electrons in the filled band

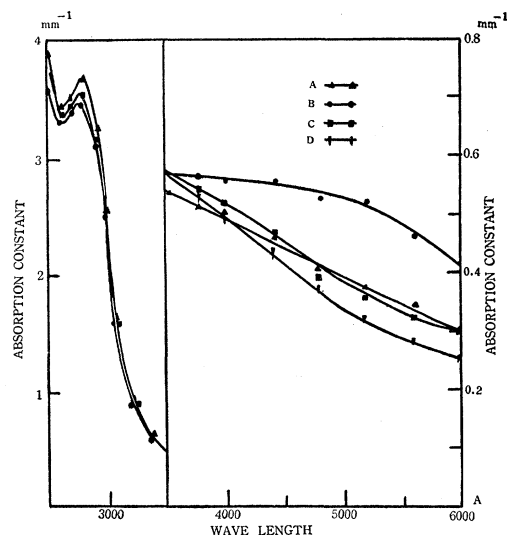


FIG. 7. (A) Absorption curve before irradiation with ultraviolet light; (B) after irradiation for 90 minutes; (C) after warming at 107°C for 3 minutes; (D) after warming at 210°C for 3 minutes.

can be easily raised to the empty localized levels with the absorption of light. Whether or not, in a case of MgO, hole or electron conduction occurs cannot be deduced since, at the moment, the experiments do not clearly indicate the signs of the charge carriers. Although it was found that the various peaks in the afterglow are accompanied by the disappearance of the absorption bands which appear in magnesium-colored

crystals, the determination of the electronic model of the luminescent processes requires more experiments.

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Elastic Moduli of Tin at the Superconducting Transition

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A composite oscillator technique was used to measure the elastic moduli of tin in the normal and superconducting states. The experiments were performed on single crystals at about 50 kc/sec. A difference in moduli was observed, indicating that the velocity of sound is less in the superconducting than in the normal state. At 3.7°K the relative change at the superconducting transition is about 4 parts in 10^6 for the longitudinal modulus S_{11} and about 6 parts in 10^6 for the torsional modulus, $2(S_{44}+S_{66})$. These relative changes increase with decreasing temperature. At room temperature, the adiabatic modulus S_{11} was found to be 1.55×10^{-12} cm²/dyne, and $2(S_{44}+S_{66})$ was 9.4×10^{-12} cm²/dyne.

I. INTRODUCTION

MANY experiments have been carried out that indicate no change in elastic properties of tin at its superconducting transition.¹⁻³ Nevertheless, a change of approximately one part in 10^5 is predicted by thermodynamics.⁴ An experimental determination was undertaken with sufficient accuracy to verify this change. Tin was used as the superconducting material, and the elastic moduli were determined by a resonant frequency method. A precision of about one part in 10^6 was obtained in measuring the difference in resonant frequency between the superconducting and normal states. The measurements show that the velocity of both longitudinal and transverse sound is less in the superconducting than in the normal state. The magnitude of the relative velocity change is dependent on crystallographic orientation and on the temperature and amounts to several parts per million near the transition temperature.

II. EXPERIMENTAL TECHNIQUES

The elastic moduli were determined by a composite oscillator technique using a single-crystal cylinder of tin glued coaxially to a piezoelectric quartz crystal.⁵ The resonant frequency of the composite was compared with the frequency of a second quartz crystal which served as a standard. By using similar quartz crystals and by carefully adjusting the length of the tin crystal, a small difference in frequency was obtained between the standard and the composite. This difference in frequency was measured in both the normal and superconducting states. The change in the difference frequency was used to calculate the change in the elastic moduli of the tin. This method eliminated the need for an accurate determination of the absolute frequency.

A schematic diagram for the frequency measurement is shown in Fig. 1. Both the composite and standard quartz crystals were in a vacuum enclosure in the helium cryostat. Each was connected to a separate amplifier immediately at the top of the cryostat. The crystals served as filter elements⁶ in the positive feedback loops of the amplifiers. The oscillators, thus formed, operated at approximately the resonant frequencies of the crystals. The two oscillator frequencies were mixed and filtered to give the difference frequency,

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† The work described in this paper, which has been presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy, was carried out in the Institute for the Study of Metals of the University of Chicago.

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² McLennan, Allen, and Wilhelm, *Trans. Roy. Soc. Can. III* **25**, 13 (1931).

³ H. Bommel and J. L. Olsen, *Phys. Rev.* **91**, 1017 (1953).

⁴ D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952), p. 76.

⁵ S. Quimby, *Phys. Rev.* **25**, 558 (1925).

⁶ W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Company, Inc., New York, 1946), p. 491.