RADIATION EFFECTS in GLASS and OTHER MATERIALS

Highlights of the 1962 Conference

By Paul W. Levy

IF the success of a meeting is judged by the number of times a session chairman is forced to terminate discussions, the "1962 Conference on Radiation Effects in Glass" must be considered exceedingly successful. This conference was held in Rochester, N. Y., on April 12th and 13th at the Dryden Theater of the Eastman House of Photography. It was designed to bring together persons actively working in this field which actually includes many materials in addition to glasses. Glass technologists and especially glass physicists have always had considerable interest in crystals that are basic glass-forming materials, e.g., SiO_2, Al_2O_3, etc. Consequently, a large fraction of the papers presented dealt with these substances. This interest also stems from the fact that the coordination of the atoms in many crystals persists as short-range coordination when they are incorporated in glasses. In fact, at this conference, glass-forming crystals were the subject of almost half of the papers presented. Also, more than half of these papers, i.e., one fourth of the total, were concerned with electron spin resonance in natural or synthetic quartz. An introduction to the subject of ESR was given by O. R. Gilliam of the University of Connecticut, who also presented some recent results on the numerous paramagnetic centers found in irradiated Al_2O_3. It appears that practically any variation in radiation conditions produces a new center in this substance. However, none of them have been worked out in complete detail.

The first of four presentations on electron spin resonance in quartz was given by J. H. Anderson of the University of Pittsburgh and J. A. Weil of Argonne. Three resonances are formed when Ge-doped quartz is irradiated with x rays and some of these correlate with an optical absorption band at 2900 Å. These centers are very complex and each one probably involves Ge in a Si site, and Na, Li, or Al atoms in nearby locations. They exhibit hyperfine interactions attributable to Na and Li. Conceivably, when one of these centers is formed during irradiation, it is stabilized by an alkali atom bound in close proximity to a substitutional Ge atom. An analogous center occurs in rose quartz which has been shown to contain titanium as an impurity, presumably in a silicon site. The titanium plays the same role in the ESR centers of rose quartz as the Ge does in the Ge-doped variety.

Additional studies on Ge-doped quartz were conducted by J. H. Mackey of the Mellon Institute. Four centers were formed by irradiation and studied at liquid-nitrogen temperature. From the "g" values one concludes that two are "electron" and two are "hole" centers. The hyperfine structure of the hole centers indicates they are associated with Al^{27} impurity while at least one of the electron centers shows hyperfine interaction with Si^{29}.

To give further emphasis to the role of impurities in oxides, J. E. Wertz and P. Auzins of the University of Minnesota presented a survey of the various ESR centers found in magnesium oxide (MgO) which could be attributed to impurities. Particularly interesting was their classification of different types of ESR centers according to the behavior of the impurities. The properties of two centers which apparently involve defects in the SiO_2 crystal structure were described in two talks given jointly by R. A. Weeks of ORNL and J. G. Castle, D. W. Feldman, and P. G. Klemens of the Westinghouse Research Laboratories. That these centers do not directly involve impurities is demonstrated by the hyperfine interactions and the orientations of the principal axis of the g-tensor. The relaxation of these centers is described by a single exponential at

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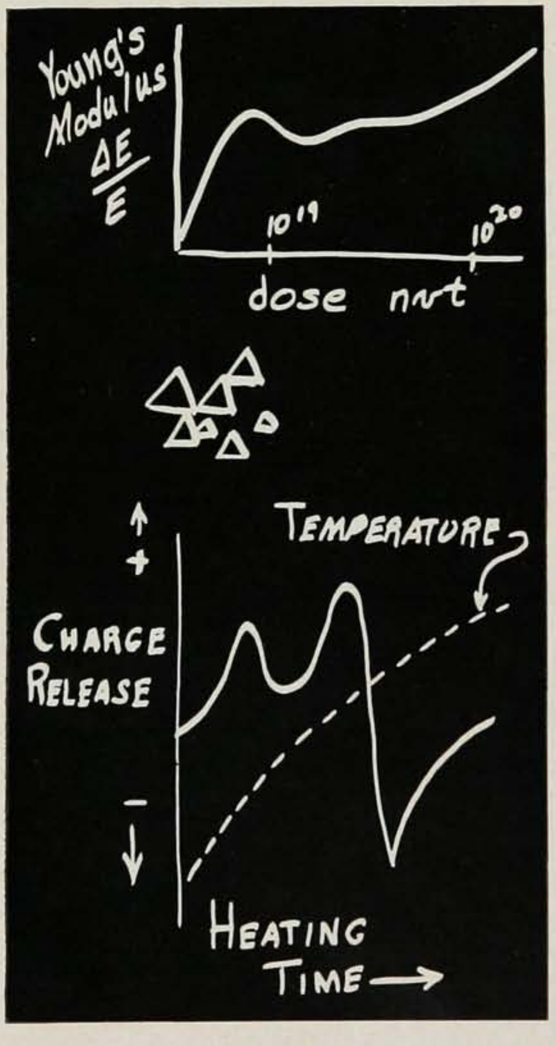
any temperature. The temperature dependence of this exponential is explainable by the addition of terms from spin-spin relaxation, single-phonon emission and absorption, and two-phonon or Raman scattering. In addition to terms in the usual expression for the relaxation time, namely $1/\tau = A + BT + CT^7$, the data in the 4° to 40°K region require that a term proportional to T^3 be included, which then is the dominant term in this region. This T^3 term is attributed to the "loose binding" between the paramagnetic center, or one atom in the center, and the lattice.

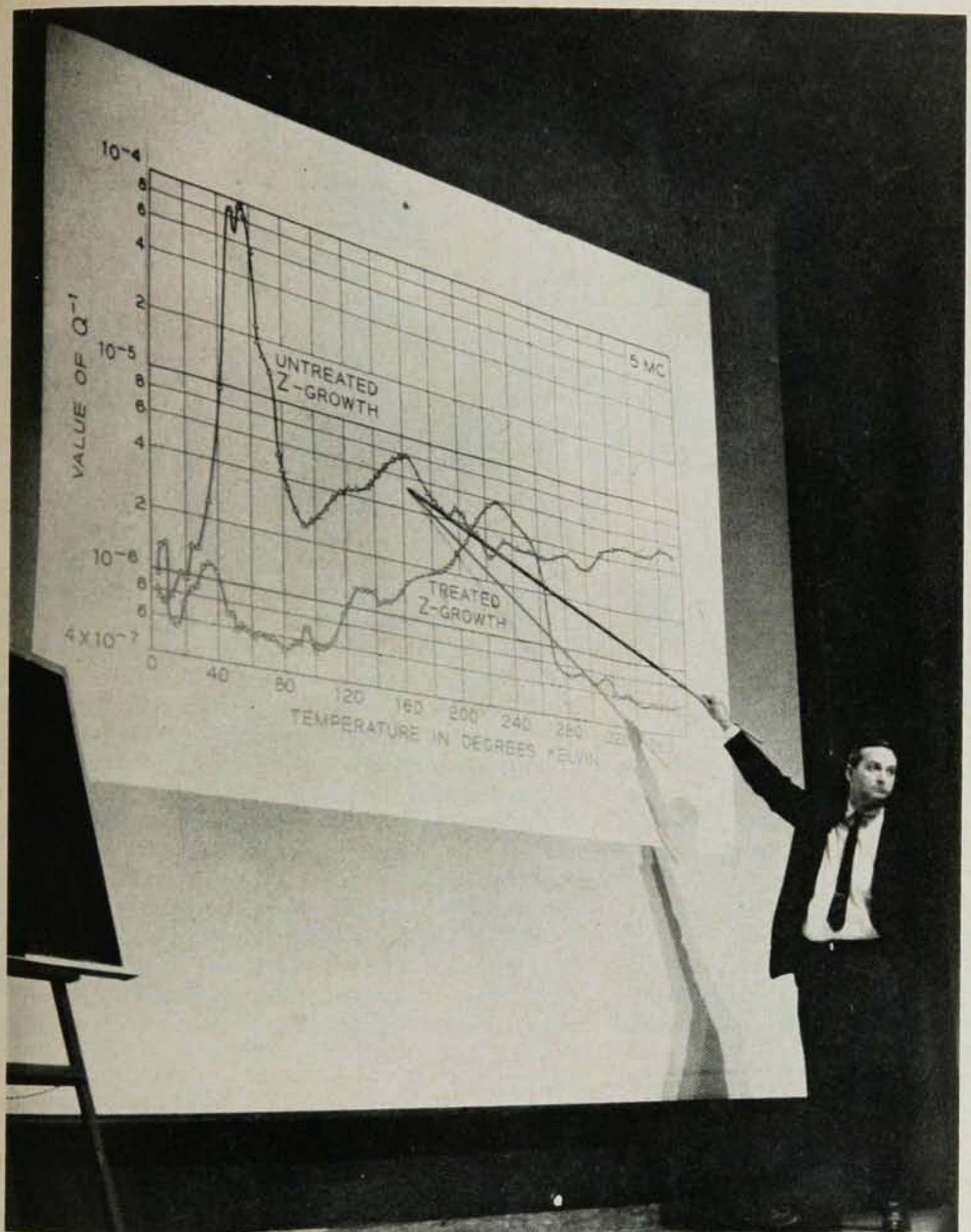
It is now well established that when energetic particles, such as fast neutrons, eject atoms from their normal positions in a crystal or glass lattice the recoils produce a region of interstitials, vacancies, and perhaps configurations of more complicated defects, along their trajectory. The author of this report refers to these regions, i.e., the entire region affected by the radiation-damage event, as Wigner regions. Associated with each region will be some degree of strain which will scatter light. Some time ago R. Maurer detected such regions in fused silica and concluded that the scattering regions were cylindrical. A re-examination of Maurer's result was described by M. Goldstein of the Ford Motor Company who concluded that the cylindrical scattering model was inadequate. Measurements of light scattering from heavily neutron-irradiated quartz crystals made at Reading University, England, were described by J. Whitehouse, who is now at Purdue. While it is clear that there is light scattering attributed to radiation-damage regions, the measurements are complicated by luminescence from radiation-induced defects. If these luminescence centers are removed by heating to near the α-β transition, one can still detect considerable light scattering. However, the intensity-versus-wavelength dependence is consistent with scattering from single point defects. This suggests that during the heat treatment the individual defects in the Wigner region have diffused apart.



The last session of the opening day was devoted to the effects of radiation on mechanical properties. One particularly interesting experiment was carried out by J. C. King and D. B. Fraser of the Bell Telephone Laboratories. They irradiated two crystal resonators simultaneously, one made from natural quartz and the other from synthetic material, and monitored the "Q" and resonant frequency during irradiation. The frequency increased linearly and the "Q" decreased linearly with flux. After irradiation, both samples behaved similarly to poor-quality resonators which contain some regions slightly out of line with the remainder of the crystal. (Appropriately enough, the Bell Laboratories presentation was the only one interrupted by the inevitable "urgent long-distance phone calls".)

An extensive study of the effects of neutron irradiation on the elastic properties of glasses containing boron was reported by J. Paymal and P. LeClerc of the Saint Gobain Research Center in Paris, France. In addition to other measurements, they made a detailed study of the variation of Young's modulus, as a function of neutron dose, for numerous glass compositions. For example, in Pyrex the modulus increases, while in lead glass it decreases with increasing irradiation; surprisingly, the modulus and length first increase, then decrease slightly and then rise monotonically as the dose is increased. From changes in these and other properties they concluded that, typically, glass goes through five stages as the neutron exposure is increased. These are, in the order of increasing dose: (1) interstitial-atom effects, (2) thermal-spike effects, (3) displacement-spike periphery effects leading to a compacted structure, (4) displacement-spike effects similar to thermal quenching, and (5) chemical effects resulting from the presence of nuclear-reaction products.

Using a combination of x-ray and electron-microscope techniques, S. Weissmann of Rutgers has investigated quartz irradiated with 10^{19} to 10^{20} nvt fast neutrons. First, he has determined the principal strain directions and magnitudes. In quartz plates these vary in a manner which is related to the orientation of the largest surfaces. This result is explained by assuming that point defects diffuse preferentially and easily along open c-axis channels. Secondly, electron-microscope studies



J. C. King discusses the "*Q*" of two varieties of artificial quartz.

indicate that interstitial oxygen and silicon atoms cluster into dislocation loops roughly 200 Å in diameter. In the most heavily irradiated samples these loops coagulate into hexagon-like networks. Obviously Weissmann's results evoked considerable interest among the conference participants.

THE second day of this meeting on radiation effects in glass began with a review of the radiation-damage studies on quartz and silica carried out at Reading University, England, and was given by E. W. J. Mitchell. A large fraction of this work has been published but has now been supplemented by recently completed computations on atomic displacements caused by electron bombardment. In particular, it was shown that defect formation in fused silica is consistent with an unusually low-threshold displacement energy. Mitchell also described the discovery of triangular-shaped regions, which he called trigons, of darkening or coloring that are found in heavily irradiated quartz.

Next was F. C. Hardtke of Argonne who presented the first of two papers on "electrical properties of irradiated glass". When glass (containing CaO, B_2O_3, and Al_2O_3—"Cabal glass") is irradiated with gamma rays and subsequently heated with a temperature gradient across it, electrical charges are released. The total charge release is proportional to the temperature gradient across the sample. Also, it is markedly influenced

J. E. Wertz, P. M. Wright, and E. W. J. Mitchell.

by the surroundings of the sample during irradiation. This is readily explained: the trapped charges result from ionization by Compton electrons which originate in the sample and its surroundings. The second paper on electrical properties was presented by E. Lell of Bausch and Lomb, who, in collaboration with R. A. Weeks at ORNL, measured the electrical conductivity and the dielectric constant of several glasses. While the conductivity is modified by irradiation, it is not clear what mechanism is responsible. The dielectric constant of the glasses was unaffected by doses up to 10^8 R; however, loss tangents were increased by factors of roughly five at 50 counts/sec and 1.1 at 10^4 counts/sec.

Much of the remainder of the meeting was devoted to various aspects of color centers in glass. This sequence was initiated by Adli M. Bishay of the American University in Cairo and K. R. Ferguson of Argonne National Laboratory. Their experiments relate the colorability of glasses to the glass structure. A related result, which could be very useful, is that the ultraviolet transmission of certain glasses is greatly enhanced by preparing them under reducing conditions. The results of a careful study of the coloring of lead-silicate glasses by gamma rays were presented by R. S. Barker and D. A. Richardson of the Pilkington Brothers, Lathom, Lancashire—one of Britain's largest glass manufacturers. They found that the induced absorption can always be resolved into two Gaussian-shaped absorption bands, that the intensity of each band increases with dose as the superposition of two saturating exponentials, that one exponential saturates at 10^6 rads and the other at 10^8 rads, and that the thermal history of the glass markedly affects its colorability. They also found that the bleaching follows an equation which could be derived from the assumption that electrons are thermally untrapped from color centers as well as from other traps which are much more numerous.

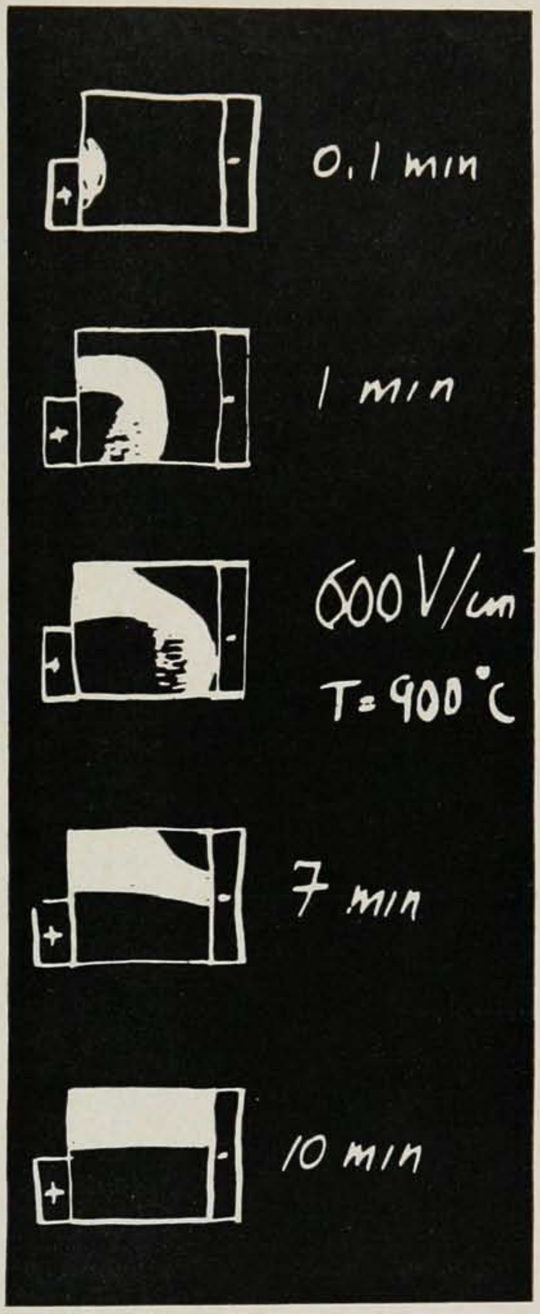
R. S. Barker, A. Smakula, and J. A. Aboaf.

A pair of papers by J. S. Stroud and R. F. Tucker of the Corning Glass Works provided very clear information on the nature of the optical absorption and ESR spectra of some binary glasses. From studies of a 75% SiO_2, 25% Na_2O glass doped with Ce^{3+} and Ce^{4+}, one can show that the radiation-induced absorption bands near 4400 Å and 6200 Å are caused by trapped holes. In glasses containing Ce^{3+} the holes are more readily trapped on the Ce^{3+}—forming a band at 2500 Å—than on the hole traps giving rise to the 4400-Å and 6200-Å bands. This clearly demonstrates the mechanism whereby cerium prevents glass from being colored, in the visible-light region, by radiation.

Annealing studies on the absorption bands formed by reactor irradiation of pure fused silica were described by P. W. Levy of Brookhaven National Laboratory. When the colored silica is heated, the absorption is decreased, but, after any annealing period, some of the color removed can be restored by irradiation with purely ionizing radiation such as gamma rays. By sufficient irradiation with purely ionizing radiation, the coloring saturates and the saturation coloring can be used as a measure of the defect concentration. Using this technique, it was found that, above 300°C, both the color center and defect concentration decrease approximately linearly with temperature. Annealing to 550°C removes all of the reactor-induced color but still one third of the defects remain.

Certainly one of the most interesting presentations was by J. Lietz of the University of Hamburg, West Germany. He showed movies of the formation of color centers in quartz by electrolysis. His samples were placed in a furnace near 1000°C and subjected to potential gradients of about 1000 V/cm. A variety of crystal orientations and electrode configurations were utilized. In one experiment a crystal was oriented with its *c*-axis perpendicular to the electrodes. The cathode covered all of one end and the anode about half of the other. When the potential was applied, a colored region spread into the entire crystal from the anode, but, after it had spread about halfway through the sample, a new colorless region formed at the anode and proceeded into the crystal. This colorless region was confined to the half of the crystal in contact with the anode. It appears that these electrolytic coloring phenomena are related to the migration of an impurity atom, e.g., sodium, which is a necessary constituent of some of the color centers.

The last speaker was V. Garino-Canina of the Saint Gobain Research Center. He described techniques used to make thermoluminescence measurements on very pure silica glasses containing controlled amounts of Ge, Al, Na, or Ce impurity. One of these glasses, which contains Ge, Al, and Na, and which must be carefully prepared, posesses a "glow" peak at 317°C which decays very slowly at room temperature. He suggested that a dosimeter could be made from this glass which could detect 100 mR and be approximately linear to 10^4 R.



As this report of the conference was being completed, a cablegram was received from Paris stating that Garino-Canina died of a heart attack on May 29, 1962. He was one of the world's foremost glass physicists; his death is a grievous loss to his friends and colleagues and to the scientific community.

The conference was organized by a committee consisting of R. A. Weeks of ORNL, the chairman, N. J. Kreidl of Bausch and Lomb, and P. W. Levy of Brookhaven. A great deal of credit for the success of the meeting must go to the Bausch and Lomb people, especially N. J. Kreidl and J. L. Rood, who made all of the local arrangements.