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Letters to the Editor

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The Metamict State

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IN a preliminary report on the behavior of a number of insulators exposed to energetic neutrons within a nuclear reactor,[1] it was reported that large changes in physical properties had been observed in diamond, silicon carbide, quartz, and vitreous silica. These property changes and their behavior seemed similar to the property changes associated with the metamictization of minerals,[2] which is attributed to the passage of alpha particles emitted from their own radioactive content. The substances previously examined and a number of others have now been exposed simultaneously in a nuclear reactor at a tempertaure believed to be above room temperature but below 100°C. An x-ray examination of these substances has now been completed and suggests a rather different conclusion as to the substances susceptible to metamictization than those suggested by Goldschmidt,[3] Pellas,[4] and others. It therefore seems desirable to report the results.

As a result of the irradiation, the following substances showed no detectable change in powder pattern: beryl, germanium dioxide (α-quartz structure), germanium, silicon, corundum, and rutile; the following substances showed only the small percent increases in lattice constant given in parentheses: magnesium oxide (0.1), spinel (0.12), calcium fluoride (0.08); the following substances showed the large percent changes given in parentheses but did not show any marked diffuseness in their diffraction patterns: diamond (0.9), silicon carbide (a, 0.68; c, 0.68). In the same irradiation were present samples of quartz, tridymite, and cristobalite. Their diffraction patterns became so diffuse that it was no longer possible to measure the positions of any lines. Chrysoberyl and phenacite irradiated under similar conditions but for about half the time showed a noticeable increase in lattice constant as shown by displacement of lines in the back reflection region (θ *ca* 80 deg) of $\frac{1}{2}$ to 1 deg but there was no noticeable line broadening. On the other hand, the diffraction pattern of a sample of tridymite irradiated simultaneously was diffuse even in the forward reflection region, and no lines could be distinguished past θ *ca* 10 degs.

From these results it is clear that the effects associated with metamictization cannot be associated with a particular crystal structure or bond type. Rather, it seems necessary that the substance possess a quasi-stable vitreous (disordered) state under the conditions of irradiation. The susceptibleness to metamictization is not determined by the state present *ab initio*, but by the difficulty of recrystallization of the disordered regions formed by the traverse of energetic atomic particles, and by the difficulty with which the displaced atoms can again form bonds. The former would give rise to large changes in the x-ray diffraction pattern, the latter to large amounts of stored energy.

The x-ray diffraction patterns were taken and measured by Stanley Siegel of this Laboratory.

Notes added in proof: (1) All of the samples which were irradiated simultaneously, were irradiated in the same container for the same time. The significant neutron flux as a function of energy E is not known, but probably does not differ greatly (by more than a factor of two) from the distribution (constant/E). From a combination of theoretical considerations and experiments performed in various reactor facilities, it seems likely that most of the damage was produced by neutrons between 0.01 and 1–2 Mev. Then, if a dosage unit is defined as the damage produced in a standard substance by $(10^{18}\int_{0.01}^{1} d\ \ln E)$ neutrons/cm^2, the radiation-damage dosage of these samples was found to be about 120 units and of the chrysoberyl and phenacite about 50 units, to within the precision usually attained in such experiments (20 percent).

(2) The elastic-constant changes reported by Binnie and Liebschutz[5] for silicon irradiated for a shorter dosage than the sample reported here is taken as evidence of the recrystallization hypothesis proposed here.

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[1] Primak, Fuchs, and Day, Phys. Rev. **92**, 1064 (1953).
[2] A. Pabst, Am. Mineralogist **37**, 137 (1952).
[3] V. M. Goldschmidt, Skrifter Norske, Videnskaps-Akad. Oslo, I. Mat.-Naturv. Kl. **1**, No. 5, 51–58 (1924).
[4] P. Pellas, Compt. rend. **233**, 369 (1951).
[5] W. P. Binnie and A. M. Liebschutz, Phys. Rev. **94**, 1410 (1954).

Shape of the *F* Band

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PREVIOUS measurements by Mollwo[1] have shown that the F absorption band in additively colored alkali halide crystals has a Lorentzian shape, and it has been generally assumed that this shape is a fundamental property of the F center and independent of the method of coloration. However, several measurements on potassium chloride crystals colored by 200-kv x-rays have shown that the F band thus formed is more nearly Gaussian in shape.

Crystals were colored at both 290°K and 113°K. In the former case a maximum concentration of 10^{17} centers per cc was obtained, while at the lower temperature only 10^{16} centers per cc were formed, though it is probable that this was not a maximum concentration. The concentrations were sensibly uniform through crystals of several millimeters thickness.

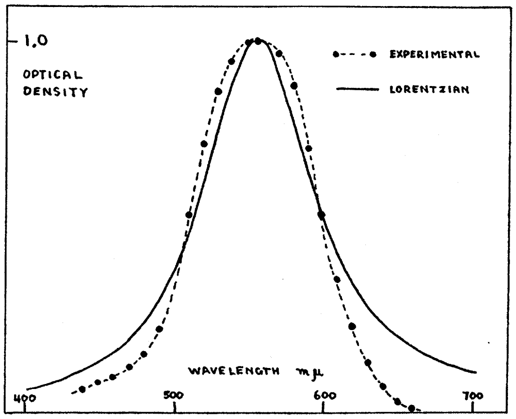

FIG. 1. The F band at 290°K.

X-irradiation creates a well-known subsidiary absorption band in the high-frequency tail of the F band, which distorts its shape at ordinates less than approximately 15 percent of the absorption maximum. At the lower temperature the F' band is also created by x-irradiation, but it can be removed by optical bleaching in F light, an unexpected result in view of the formation of the F' band in additively colored crystals exposed to F light. At room temperature only M secondary centers are created in addition to the F band, and the two absorptions do not overlap. Thus the shape of the whole of the low-frequency side of the F band can be determined at both temperatures, see Figs. 1 and 2.

On the high-frequency side, the F absorption curve is accurately Gaussian down to the 15 percent ordinate, but the equation of the low-frequency side has an index which is not two, and which appears to be temperature-dependent. At room temperature the optical density has the equation, $D=D_{\max}\exp[-(\nu_{\max}-\nu)^{2.5}]$, while at 113°K, after removal of the F' band and the recovery of the F band from bleaching,[2] the index is 2.8.

Measurements have not yet been made on additively colored crystals having a comparable number of centers, nor on x-irradiated crystals containing higher concentrations. Our results on the shape together with those on the half-width[3] of the F-band point to a significant difference between the two types of coloration.

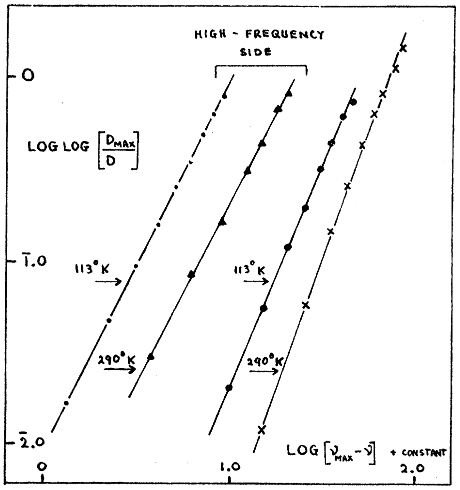

FIG. 2. A Gaussian plot of the F-band absorption.

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[1] E. Mollwo, Z. Physik 85, 56 (1933).

[2] Markham, Platt, and Mador, Phys. Rev. 92, 597 (1953).

[3] Mador, Markham, and Platt, Phys. Rev. 91, 1277 (1953).

Precipitation of Impurities at Dislocations in Heat-Treated Silicon

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WE have conducted a series of heat treatments on silicon which suggest precipitation of impurities at dislocations when the silicon is heated below 900°C. The idea that impurities segregate at dislocations below a certain critical temperature was suggested by the work of Cottrell.[1] The same idea has been applied to the interaction of impurities with dislocations in germanium by Kurtz and Kulin[2] and to the interaction of interstitial germanium with dislocations in germanium by Mayburg.[3]

The single-crystal silicon used was pulled from a quartz boat. Its resistivity before any heat treatment was approximately 8 ohm-cm, p type. The samples are heated by passing current through them in high vacuum, and the effects of the heat treatment are measured by quenching and studying changes in room temperature conductivity. The experimental setup is identical with that previously used for heat treatment studies in germanium.[3]

Any changes in room temperature conductivity σ can be ascribed primarily to changes in the concentration of acceptors N_A or donors N_D. Since the conductivity is

$$\sigma=(N_A-N_D)e\mu_p,$$

where e is the charge of a hole and μ_p is the hole mobility, an irreversible change in σ would correspond to either a continuous increase or decrease with the time of heat treatment in the concentration of either the acceptors or the donors in the sample. Our experimental arrangement is such that it is only possible that impurities are leaving the sample by evaporation. Therefore, any irreversible conductivity change we might observe would result from the loss of either acceptors or donors.

At approximately 1100°C, and also around 1300°C, we observed irreversible increases in the conductivity of an original p-type sample of 100 percent and 25 percent, respectively. The fact that these increases occur at two characteristic temperatures suggest that in this particular p-type crystal there are at least two donor impurities which can be evaporated out of the silicon.

We find that by heating a fresh sample above or below 900°C, we increase or decrease respectively the