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ANISOTROPIC OPTICAL ABSORPTION IN DEFORMED MgO (*)

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Résumé. — La principale bande d'absorption optique produite dans MgO par déformation a été trouvée constituée de deux parties, désignées bandes δ et ϵ , absorbant à 5,82 et 5,65 eV respectivement. On suppose que ces bandes sont créées par le même type de transition excitonique avec des perturbations différentes. Sous irradiation X le centre ϵ capture un électron, produisant un centre E qui absorbe à 4,07 et 5,17 MeV. Lorsqu'un seul système de glissement opère dans le processus de déformation, l'absorption E est dichroïque à 100 % indiquant la symétrie $\langle 100 \rangle$ du centre. L'axe du défaut est compatible avec l'idée que les défauts sont dus à des lacunes produites par des crans dans des dislocations-vis. Des données de traitements thermiques isochroniques sont discutées ainsi que des modèles possibles pour ces centres.

Abstract. — The prominent optical absorption band produced in MgO by deformation has been found to be made up of two parts designated δ and ϵ bands absorbing at 5.82 and 5.65 eV, respectively. These bands are presumed to arise from the same type of excitonic transition with different perturbations. Upon x-irradiation the ϵ center is found to capture an electron producing an E center which absorbs at both 4.07 and 5.17 eV. When only one slip system was operative in the deformation process the E absorption was found to be 100 % dichroic indicating $\langle 100 \rangle$ symmetry for the center. The defect axis is consistent with the view that the defects result from vacancies produced by jogs in screw dislocations. Isochronal annealing data as well as possible models for these centers are presented.

1. **Introduction.** — Ionic crystals have proven to be useful in studying the deformation process. Relatively new techniques for such studies, electron spin resonance and optical absorption, are providing answers not available by other techniques. For example, by monitoring the concentration of F^+ centers with electron spin resonance, Sibley, Kolopus and Mallard [1] found that deformation of MgO produced anion vacancies whose concentration varied linearly with the amount of deformation. Similarly, optical absorption measurements of the V^- type centers in deformed MgO [2a], indicate a linear increase of the cation concentration with deformation. For both types of vacancies the increase was found to be approximately $4 \times 10^{16} \text{ cm}^{-3}/\%$ deformation. These results are consistent with the suggestion that dislocation interactions produce vacant lattice sites.

In the investigation of Sibley *et al.* [1] the F^+ band was not resolved in their optical absorption data. However, they did find a new optical absorption band in deformed and unirradiated MgO at 5.73 eV whose intensity suggests that the production of single vacancies is not the most important effect of deformation. If one assumes an oscillator strength of one for this deformation induced absorption band in MgO one finds the concentration of defects producing this band to be $7 \times 10^{17} \text{ cm}^{-3}/\%$ deformation,

approximately twenty times as great per cent deformation as the production rate of single vacancies. In subsequent studies with deformed CaO and SrO [2b] similar deformation-induced optical absorption bands were found whose intensity varied linearly with deformation. Since these bands, designated δ bands, were all produced in the same manner and fit on a Mollwo-Ivey plot, it was suggested that they were all produced by the same type defect in the three alkaline earth oxides. It was found that the δ bands in CaO and SrO were dichroic indicating 100 symmetry for the defects producing the bands. Since these bands were not due to single vacancies, but are from a defect with 100 symmetry it was suggested that they arise from anion-cation vacancy pairs.

Support for the suggestion of vacancy pairs comes from studies of the effect of deformation on the density of crystals. Such studies have not been made in deformed MgO, but in deformed LiF, by Andreev and Smirnov [3]. When slip occurred along a single crystallographic plane they found a decrease in density which varied linearly with strain. They concluded that the density changes were basically caused by the creation of vacancy pairs during double cross slip and the mutual intersection of dislocations of various slip systems. These authors converted their relative density changes into equivalent vacancy pair concentrations and found the number produced to be $2 \times 10^{17} \text{ cm}^{-3}/\%$ deformation.

If, indeed, the vacancy pair is the fundamental

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defect produced by the deformation of ionic crystals, and the δ band is produced by the vacancy pair, these optical absorption studies should be exploited for a positive identification to give more information about its formation, interaction with other defects and finally its annihilation. To such an end we report annealing studies on single crystals of MgO deformed by compression as well as data on emission and dichroic optical absorption. It appears that the band originally designated the δ band is made up of two parts, the δ band and a second part which we will designate the ϵ band. This ϵ band is found to be dichroic and to arise from a defect with 100 symmetry. The defects producing the ϵ band capture electrons upon x-irradiation to produce a daughter which we designate as the E band [4]. Before considering the experimental details and the results we present a brief discussion on excitons since the δ and ϵ bands are presumed to arise from bound exciton transitions. We also present a brief discussion of recently published results on the E band since it is produced by the same lattice defects which produce the ϵ band.

2. Excitons. — An electron hole pair may be produced in a crystal when a photon is absorbed whose energy is slightly less than the band gap. In such a situation the electron and hole will be bound and form a neutral excited mobile state of the crystal known as an exciton. To create an exciton an electron is raised to an orbital such that the lowest excited electronic state of the crystal results. In the event the exciton is created by producing a hole on a cation adjacent to an anion vacancy a bound exciton results. The excited electron would then reside in a local level rather than a state of the crystal. In the alkali halides such a bound exciton produces the α band. In KBr for example the lowest energy exciton occurs at 6.63 eV [5] while the α transition occurs at 6.17 eV. If the exciton transition is perturbed by an F center, that is, if the anion vacancy captures an electron, the transition, referred to as the β band, occurs at 6.45 eV [6]. The neutral F center does not provide as large a perturbation as the anion vacancy. It should be noted that the α and β transitions are identical except for the amount of perturbation. When the vacancy which produces the α band captures an electron the F band is produced. Thus the F band can be thought of as a daughter of the α band. This is the sense in which we use the term daughter to relate the ϵ and E bands. The discovery of the α and β bands and the interpretation of their origin is due to Delbecq, Pringsheim and Yuster [7]. Timusk [8] has measured the temperature dependence of the half-width of the emission band of the α center in KBr. His results suggest that lattice interactions of the α center in the excited state are similar to those of the F center in the ground state, indicating the localization of the electron in the α transition. The emission energy of the α center in KBr is 2.47 eV. This is one of the

highest Stokes shifts known. For later comparisons we note that the oscillator strength of the α transition was found to be 1.1.

3. The E center. — In an earlier investigation [2a] of deformed MgO, specimens were used such that optical absorption studies could be made in all three $\langle 100 \rangle$ directions. A crystal was deformed 0.84 % in compression such that only one slip system was operative. The crystal was compressed along its longest axis which we shall designate $\langle 001 \rangle$. Following x-irradiation the spectra shown in figure 1

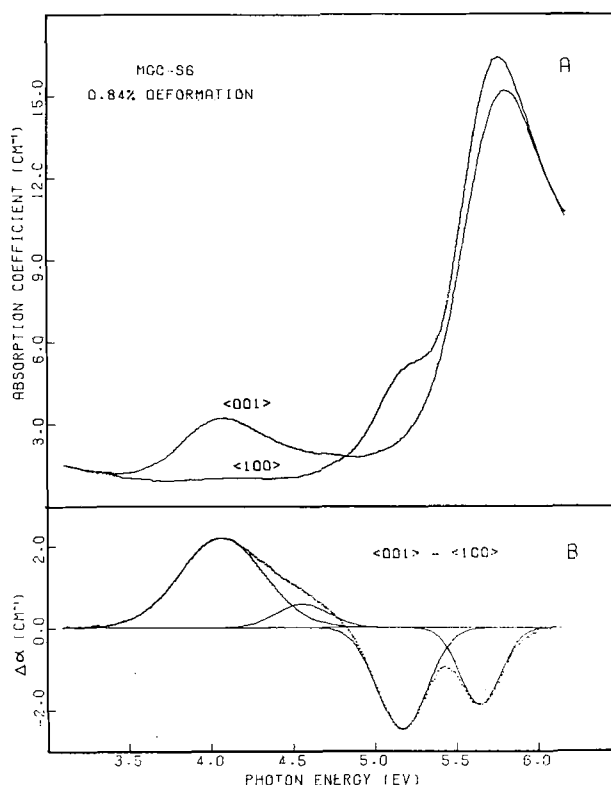


FIG. 1. — A) Polarized absorption measurements obtained with the electric vector of the incident light in the direction indicated. The crystal was compressed along the $\langle 001 \rangle$ axis and light was incident along the $\langle 010 \rangle$ direction. B) A dichroic absorption plot obtained from subtracting the curves of part A. Four peaks are fit by Gaussian plots with maxima at 4.07, 4.56, 5.17 and 5.65 eV and widths of 0.60, 0.39, 0.36 and 0.30 eV, respectively.

were obtained with the light transmitted along $\langle 010 \rangle$. In part A the curve designated $\langle 001 \rangle$ was obtained with polarized light with the electric vector along the $\langle 001 \rangle$ direction. Similarly the second curve was obtained with the electric vector along the $\langle 100 \rangle$ direction. In figure 1B we see a dichroic plot obtained by subtracting the curves of part A. We see four peaks, all of which can be fitted with Gaussian plots, located at 4.07, 4.56, 5.17 and 5.65 eV. By dichroic absorption and bleaching measurements along all three axes we found that the 5.17 and 4.07 eV bands arise from the same defect which we call the

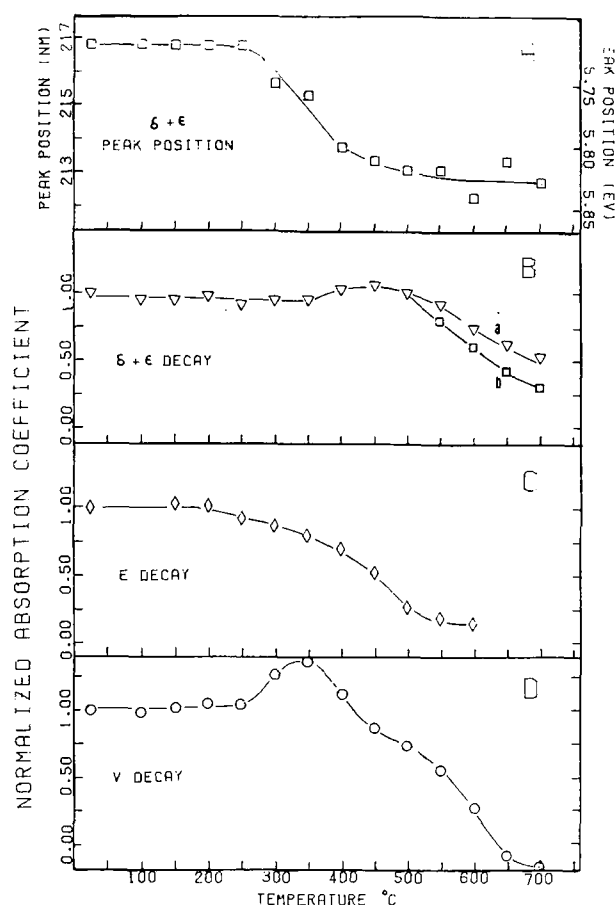


FIG. 2. — A) An isochronal plot of peak position as a function of temperature for the deformation induced optical absorption bands $\delta + \epsilon$. B) Normalized absorption coefficient for the $\delta + \epsilon$ bands as a function of annealing temperature. Above 500 °C curve b indicates the δ band alone with a constant ϵ absorption subtracted, while a is the sum of $\epsilon + \delta$. C) and D) Isochronal plots of the normalized absorption coefficients for the E and V band decay.

E center. We shall refer to the 5.17 eV transition as the E_σ transition since it arises from the transition moment parallel to the axis of the defect and to the 4.07 eV transition as the E_π band since there are two such transitions perpendicular to the axis of the defect. The dichroism from the E center is found to be essentially 100 % with the axis of the defect along a $\langle 100 \rangle$ direction. The 4.07 eV transition was originally observed by Sibley *et al.* [1].

The axis of the E center lies along the direction that one would expect to obtain dislocation dipoles from the motion of screw dislocations containing jogs. If the jogs are small enough one gets non-conservative dislocation motion and rows of vacancies or rows of interstitials are formed. Narayan and Washburn [9] have concluded from their electron microscope observations that vacancy type dipoles predominate in deformed MgO. Thus it appears that the E center arises from a vacancy cluster of $\langle 100 \rangle$ symmetry that has captured one or more electrons. Clark and Crawford [10] have reached

a similar conclusion regarding the E center in alkali halides.

When the deformed, irradiated crystal of figure 1 was bleached in the V band region (2.3 eV) to release holes it was found that the E_π and E_σ transitions decayed at the same rate while simultaneously a band grew in at 5.65 eV. Similarly, it was found that upon bleaching the E_π band the V^- and E_σ bands decayed simultaneously and a band grew in at 5.65 eV. It was suggested that the defect producing the 5.65 eV absorption, which we now call the ϵ center, captures an electron and produces the E center. The E center can be destroyed by hole capture upon bleaching with the V band, or by electron release by bleaching the E band.

In the earlier work we were puzzled that V^- centers bearing a negative charge would capture an electron. Subsequent work [11] has shown that most of the V centers are V_{Al} or V_{OH} centers which are neutral and hence do not repel the electron.

4. Experimental procedure. — The crystals were grown at the Oak Ridge National Laboratory and obtained through the courtesy of Drs. C. T. Butler and W. A. Sibley. Typical analyses have been published elsewhere [12]. The specimen dimension were approximately $3 \times 4 \times 7$ mm³. This dimension was used so that absorption measurements could be made in all three $\langle 100 \rangle$ directions. After cleaving, the crystals were polished in boiling orthophosphoric acid for three minutes, then rinsed in room temperature acid, methanol, ether and distilled water.

The crystals were deformed in compression along the longest $\langle 100 \rangle$ axis in an Instron testing machine with a crosshead speed of 0.05 cm/min., corresponding to an approximate strain rate of 10^3 s⁻¹. For x-irradiation the crystals were placed 4 cm from a copper target operated at 40 kVp and 25 mA for 25 min. through each of the faces perpendicular to the shortest $\langle 100 \rangle$ axis. Within one minute after completion of the x-irradiation, optical absorption data were obtained at room temperature on a Cary Model 14 spectrophotometer. For the of dichroism, measurements Polacoat 105 ultraviolet polarizers were placed in both the reference and sample ports of the spectrophotometer.

All absorption data were taken and stored on paper tape by a data acquisition and analysis system built around a Hewlett Packard 2114 A computer [13]. When it was necessary to return a sample to its pre-x-irradiated state following absorption measurement it was bleached with a 200-watt Hg-Xe lamp filtered with a glass lens.

Etching to reveal the slip systems was performed with a solution of five parts saturated NH_3Cl , one part concentrated H_2SO_4 and one part distilled water. Crystals were etched at room temperature for fifteen minutes then rinsed in methanol and finally in ether. The annealing experiments were performed

between room temperature and 700 °C in argon atmosphere in a muffle furnace. For the isothermal experiments the crystals were held at temperature ± 3 °C, for ten minute intervals.

For the bending experiments, the crystals were cleaved to a thickness of about 0.5 mm and then thinned to about 0.25 mm in H_3PO_4 at 180 °C, followed by the above rinsing procedure. The crystals were then bent backwards and forwards 15 times about a 5 cm radius [9].

5. Experimental results. — From figure 1 it can be seen that there is more than one optical absorption band in the region of 5.7 eV. By monitoring this peak position as a function of temperature we can see a definite change as one peak begins to anneal. This is illustrated in part A of figure 2. It can be seen that in the region from 250 °C to 500 °C the peak shifts from 5.72 eV (216.8 nm) to 5.82 eV (213 nm). Designating the 5.82 eV band as δ and the 5.65 eV band from figure 2 as ϵ we see that the composite band at 5.72 eV is simply an average of these two.

In figure 2B we have an isochronal plot of the normalized absorption coefficient of the deformation induced optical absorption band. Thus, initially we have a plot of the δ and ϵ bands and after approximately 500 °C a plot of the δ band alone. Even after an anneal at 800 °C there is a small amount of ϵ band remaining. This is illustrated in figure 3.

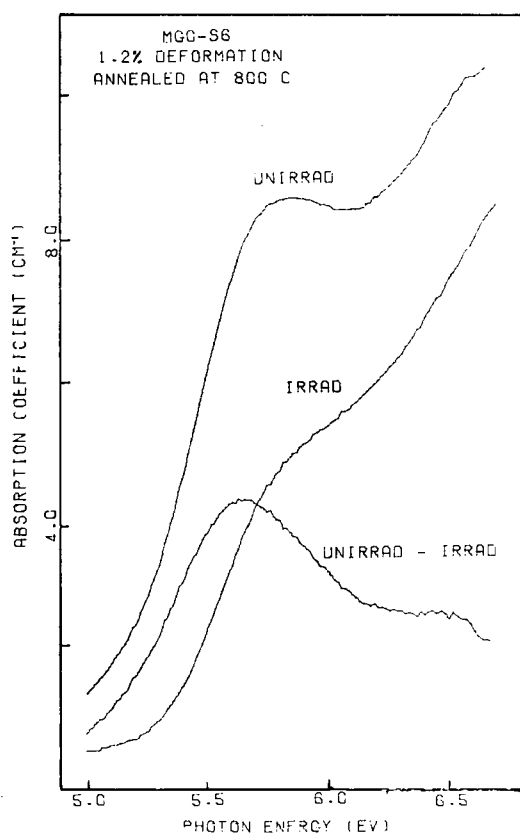


FIG. 3. — Absorption of a crystal deformed 1.2 % and annealed at 800 °C before and after x-irradiation.

Thus in figure 2B the lower curve, designated b, is obtained when the remaining ϵ band is subtracted. These data are less accurate above 600 °C because, as seen in figure 3, the δ band appears on the shoulder of another band growing with increasing temperature. Unfortunately this band is beyond the limit of the spectrophotometer employed. The difference plot of figure 3 indicates a band in the region of 6.5 eV. This has been observed with difference plots from several preceding anneals.

In figure 2C we have an isochronal plot of the normalized dichroic absorption of the E band. This is the temperature dependence of the data given in figure 1B and is valid for the decay of E_π (4.07 eV) and E_σ (5.17 eV). It should be noted that it was necessary to re-irradiate after each anneal to repopulate the electron traps. Otherwise the band is destroyed by capturing holes released from V centers. The decay of the dichroism of E_π does not result from an increase of $\alpha_{<100>}$ and a decrease of $\alpha_{<001>}$ until they are equal, rather $\alpha_{<100>}$ remains zero and $\alpha_{<001>}$ approaches zero, indicating that decay results from the break up of the defect rather than its rotation and migration to a sink. The temperature range in which this occurs is consistent with the range in which the deformation band shifts, illustrated in figure 2A.

In figure 2D we have an isochronal plot of the V^- band. These data are normalized with the V^- absorption produced by the deformation process, not the total V band absorption in the specimen. Recall that the V band results from a hole trapped adjacent to a magnesium vacancy. Thus we use the concentration of V centers as a monitor of the cation concentration. Again it should be noted that it was necessary to reirradiate the specimen after each anneal to repopulate the electron traps. It can be seen that in the range from 250 to 350 °C the concentration of cation vacancies increases. Thus it appears that the defects which produce the E band in the unirradiated crystal and the E band in the irradiated crystal break up by the release of cation vacancies.

6. Discussion. — As magnesium oxide is deformed it appears that *at least* two types of vacancy clusters are formed. The first, which we have referred to as the δ center, produces an optical absorption band at 5.82 eV. The second type of vacancy cluster, referred to as the ϵ center, produces a band at 5.65 eV which is dichroic, indicating that the ϵ center has $<100>$ symmetry. We suggest that both the δ and ϵ absorption bands come from the same type transition, an electron is excited from an adjacent oxygen ion into the adjacent vacancy complex, forming a bound exciton. Presumably the ϵ absorption comes at a slightly lower energy because there is a larger perturbation to the system.

Just as the α center in the alkali halide captures an electron and becomes the F center, in MgO it appears

that the ϵ center captures an electron and becomes an E center. Thus to utilize annealing data to help determine the character of the δ and ϵ centers we examine, in addition to the isochronal plot of the decay of the (δ and ϵ) « band » also the decay of the E and V bands.

At approximately 250 °C as the ϵ and hence E bands begin to disappear the concentration of V centers increases, indicating that the break up of the ϵ center may be accompanied by the release of cation vacancies. Assuming an oscillator strength of 0.1 [1] for the V band the increase of figure 2D corresponds to the release of 3×10^{15} cation vacancies/cm³. While the ϵ center is breaking up and the V band is increasing the concentration of $\delta + \epsilon$ centers (Fig. 2B) is unchanged. This may indicate that δ centers are left following the break up of the ϵ band or that similar bound excitons are produced by the defects left as the ϵ centers decay.

From figures 2B and 2D it can be seen that as the V band stops increasing the δ band begins to increase. This may indicate that at this temperature, approximately 350 °C, the released cation vacancies migrate to anions to form clusters, thus increasing the δ band. Apparently this process continues out to much higher temperatures because the V band intensity and hence cation concentration drops below that number put into the crystal by deformation, indicating that cations used for compensation are clustering.

In an earlier work we attributed the decrease of the δ band upon x-irradiation to the capture of electrons by vacancy pairs. We now see that the decrease was produced by the capture of electrons by ϵ centers, not δ centers. From figure 3 we see that even after annealing at 800 °C there is a decrease in optical absorption in the δ band region upon x-irradiation. However, upon subtracting the absorption after irradiation from that before one sees a peak at 5.05 eV indicating ϵ centers that are stabilized and not decaying. Support for this view comes from the fact that the difference peak is the same height following anneals of 700, 750 and 800 °C. We suspect that the center is stabilized by the presence of impurities. The position of the ϵ band leads us to believe that it results from the same transition as the δ band except a larger vacancy cluster provides a slightly greater perturbation to the transition, that is 5.65 eV rather than 5.82 eV. From figure 1 we see that the ϵ center is anisotropic with its axis along a $\langle 100 \rangle$ direction. In the same figure it can be seen that the E band, resulting from electron capture by the ϵ center, also has 100 symmetry. As indicated earlier, this is demonstrated in a previous publication [2a] by dichroic absorption and bleaching studies through all three faces of the crystal. Thus the ϵ center is a vacancy cluster with 100 symmetry that is an electron trap. Annealing studies indicate that the E band does not lose its dichroism, thus the vacancy cluster

does not rotate, but is apparently annihilated by breaking up. Further evidence for this comes from the annealing studies of the V band which increases slightly as the E band decays. This suggests that magnesium vacancies are released as the E band decays. One clue to the identity of the ϵ center comes from its method of production and the particular $\langle 100 \rangle$ direction along which it is aligned. From an earlier study in which the optical anisotropy has been correlated with the dislocation bands on the crystal face we know that the $\langle 100 \rangle$ direction of the ϵ center is the same direction along which vacancies are produced from jogs in screw dislocations.

It was suggested earlier [2a] that the E center and hence the ϵ center might result from a linear trivacancy with oxygen, magnesium and oxygen vacancies. This would satisfy the requirements of symmetry and ability to trap electrons. It could be considered an F⁺ center perturbed by a vacancy pair. The transition energies of the E center appear compatible with such a defect.

In earlier work on CaO and SrO dichroism was reported in the δ bands, indicating defects with 100 symmetry. A careful subtraction of these bands in the literature indicates that the difference plots peak at slightly different energies from the unsubtracted peaks. We suggest that this indicates the presence of ϵ and δ bands in these systems. Even though in MgO we have found the $\langle 100 \rangle$ anisotropy to be associated with the ϵ band rather than the δ band we still find the vacancy pair to be a reasonable suggestion for the origin of the δ band. The lack of dichroism in the δ band may result from the ease with which the magnesium vacancy may rotate about the oxygen vacancy during the formation process.

Luminescence studies of the δ and ϵ bands are in progress. The emission is found to peak at 3.0 eV when the system is excited with photons of energy 5.76 eV. The width of the absorption and emission bands are approximately equal. Additional absorption studies also appear to be fruitful in unravelling the defects produced by deformation. For example, the band at 4.56 eV in figure 1 has been observed in a number of crystals to have about the same relative height as the E _{π} band (4.07 eV) as shown. However, when we deformed a thin crystal by bending rather than by compression the 4.56 eV band was considerably larger relative to the E _{π} band. Other bands have been observed in the range of 4 to 6 eV upon annealing and irradiating the deformed crystals. These will be the subject of a later report.

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