

TABLE V. Predicted U luminescence band peak positions.

Crystal	ϵ_p (eV)
KCl	4.07
KBr	3.58
RbCl	3.79
CsBr	2.89

It is possible to predict the peak positions of the U -center luminescence band from the consideration of the Stokes shift. To date, however, no emission study of the U center has been made, presumably because of the relative unstability of the U center when irradiated by ultraviolet light. In the case of the F center, the Huang-Rhys factor for absorption and emission does not differ. If we assume that the same is true in the case of the U center, the Stokes shift between the emission and absorption bands will be given by $2\hbar\omega_0 S$. The estimated U emission band positions are given in Table V. Some of the problems involving the study of luminescence

spectrum of the U center have been discussed elsewhere⁶ and will not be elaborated here.

ACKNOWLEDGMENTS

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Defect Cluster Centers in MgO[†]

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A study of the production and annealing of defect cluster centers in MgO single crystals has been undertaken. A comparison of the annealing of single negative-ion vacancies in neutron-irradiated, electron-irradiated, and Mg-additively colored samples is made. The results indicate that isolated negative-ion vacancies are not mobile below 900°C, and the annealing of these defects at lower temperatures in irradiated crystals is due to interstitial migration. The broad absorption bands at 352, 573, and 975 nm and the zero-phonon lines observed in neutron-irradiated crystals, previously proposed as due to F -aggregate centers, are not observed in electron-irradiated and additively colored samples even after annealing. Therefore, there is some uncertainty whether these lines and/or bands are due to F -aggregate centers.

INTRODUCTION

COLOR centers in MgO have been studied extensively the past few years.¹⁻¹³ The most intense

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¹ F. P. Clarke, *Phil. Mag.* **2**, 607 (1957).

² J. E. Wertz, P. Auzins, R. A. Weeks, and R. H. Silsbee, *Phys. Rev.* **107**, 1535 (1957).

³ J. E. Wertz, G. Saville, P. Auzins, and J. W. Orton, *J. Phys. Soc. Japan* **18**, Suppl. II, 305 (1963).

⁴ J. E. Wertz, G. S. Saville, L. Hall, and P. Auzins, *Proc. Brit. Ceramic Soc.* **1**, 59 (1964).

⁵ I. K. Ludlow and W. A. Runciman, *Proc. Phys. Soc. (London)* **86**, 1081 (1965).

⁶ I. K. Ludlow, *Proc. Phys. Soc. (London)* **88**, 763 (1966).

⁷ R. A. Shatas and J. D. Stettler, *Bull. Am. Phys. Soc.* **11**, 811 (1966).

⁸ B. Henderson and R. D. King, *Phil. Mag.* **13**, 1149 (1966).

⁹ R. D. King and B. Henderson, *Proc. Phys. Soc. (London)* **89**, 153 (1966).

optical absorption band in these crystals whether neutron-irradiated, electron-irradiated, or additively colored occurs at 250 nm. There is little doubt that this band is due to F -type (oxygen vacancy) centers. In fact, it may be due to both positively charged F^+ centers (negative-ion vacancies each possessing one electron)¹⁴ and neutral F centers (negative-ion vacancies each with two electrons), absorbing light at about the same wavelength.¹⁵

¹⁰ J. C. Kemp, W. M. Ziniker, and J. A. Glaze, *Phys. Letters* **22**, 37 (1966).

¹¹ W. A. Sibley and Y. Chen, *Phys. Rev.* **160**, 712 (1967).

¹² M. Nakagawa and K. Ozawa, *J. Phys. Soc. Japan* **24**, 96 (1968).

¹³ E. B. Hensley, W. C. Ward, B. P. Johnson, and R. L. Kroes, *Phys. Rev.* **127**, 1227 (1968).

¹⁴ Notations after B. Henderson and J. E. Wertz, *Advan. Phys.* **17**, 749 (1968). Previous designations are F center for the one-electron oxygen vacancy, and F' center for the two-electron oxygen vacancy.

¹⁵ Y. Chen, W. A. Sibley, F. D. Srygley, R. A. Weeks, E. B. Hensley, and R. L. Kroes, *J. Phys. Chem. Solids* **29**, 863 (1968).

TABLE I. Impurity analysis.

Element	Impurity content (ppm)	Element	Impurity content (ppm)
N	2	Zr	<3
Ca	23-60	S	<2
Na	0.3-3.0	Zn	2-26
Fe	~3	P	~1
Al	30-40	S	<2
Si	15-34	B	<1
Cr	<3	Pb	<0.5
Mn	<1		

In the case of neutron-irradiated specimens, three bands at 355, 574, and 975 nm occur in addition to the one at 250 nm. Zero-phonon lines are observed at low temperatures in the vicinity of these bands, and the symmetries of the defects responsible for these lines have been determined by uniaxial-stress measurements. Ludlow and Runciman found that the zero-phonon lines at 361.5 and 1044.5 nm have $\langle 110 \rangle$ symmetry,^{5,6} and these have been referred to as due to "M-like" centers.¹⁴ King and Henderson⁹ associated the lines at 524.3, 641.7, and 648.8 nm in heat-treated samples with "R-like" centers.

In alkali halides, the *M* center (two adjacent *F* centers with $\langle 110 \rangle$ symmetry) and the *R* center (three *F* centers forming a $\langle 111 \rangle$ trigonal defect) have been positively identified.¹⁶ Furthermore, the various conditions under which these *F*-aggregate centers can be produced are well substantiated. In KCl, for instance, *M* centers can be created by forming a sufficient *F*-center concentration, by radiation or additive coloration, such that the number of *F* centers formed adjacent to one another becomes great enough to be observable. It has also been shown in KCl that *F*-aggregate centers can be thermally or optically produced at the expense of *F* centers. The primary purpose of this study is to attempt to produce in MgO the bands and zero-phonon lines attributed to *F*-aggregate centers by utilizing some of these techniques.

PROCEDURE

Unless indicated otherwise, the MgO specimens used in this work were cleaved from single crystals grown by N. Quinn of W. and C. Spicer Ltd. and contained less than 5 ppm Fe. The thicknesses of the sample plates varied between 0.15 and 5 mm. Impurity concentrations were obtained by means of wet-chemistry, flame photometry, and neutron activation. Analysis of a typical batch is tabulated in Table I. A specimen of comparable purity was also obtained from the General Electric Co. Crystals having an Fe content of about 60 ppm were procured from Muscle-Shoals Electrochemical Co.

Specimens were neutron-irradiated for periods of from 1 min to 50 h in the Oak Ridge Reactor Hydraulic

¹⁶ W. D. Compton and H. Rabin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. 16.

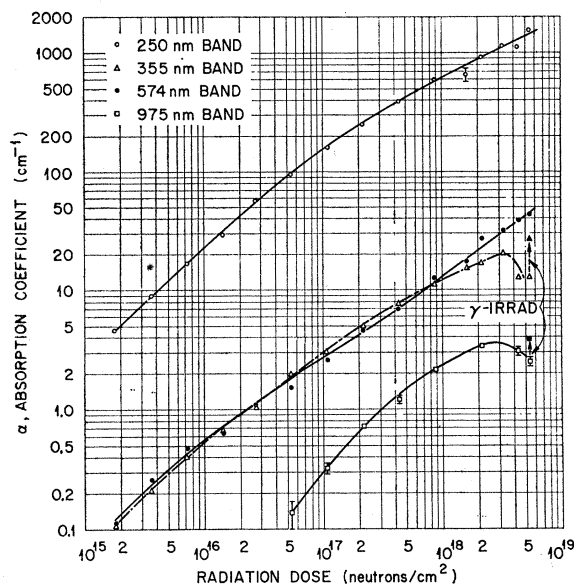


FIG. 1. Plot of absorption coefficient versus neutron dose for the bands at 250, 355, 574, and 975 nm.

Tube System No. 1-F-8 Tube 12. They were wrapped in 5 mils of cadmium foil to reduce the thermal neutron flux and were maintained at a temperature of about 50–70°C by cooling water from the reactor pool.¹¹ The flux of neutrons with energy greater than 1 MeV was measured to be 3×10^{13} neutrons/cm² sec for this facility.¹⁷ Several samples were neutron-irradiated, courtesy of B. C. Kelley, at about –120°C in the liquid-nitrogen facility of the bulk shielding reactor, where the neutron flux is 4×10^{12} neutrons/cm² sec. Specimens were also irradiated in a special water- and air-cooled holder at 50°C with 1.7-MeV electrons from a Van der Graaff accelerator. A specimen colored with an excess of Mg at 1740°C at a pressure of 4300 Torr for 5 min was kindly sent to us by E. B. Hensley¹³ of the University of Missouri. Crystals were cleaned or reduced in thickness by etching in phosphoric acid, nitric acid, or in a solution of H₂SO₄ and NH₄Cl at temperatures below 60°C, and rinsing with water. γ irradiation was carried out using a 3×10^6 R/h Co⁶⁰ source.

Optical-absorption measurements were made with a Cary spectrophotometer model 14 R. A Sulfrian cryostat was used for low-temperature measurements. Measurements of absorption bands induced by neutron irradiation were normally made after the specimens had been optically bleached for a sufficiently long time with white light to eliminate the *V*₁ (positive-ion vacancy with one trapped hole) band at 540 nm, and to obtain constant background in the uv region. The absorption coefficient for the 250-nm band was obtained in heavily irradiated crystals by measuring the absorption at the wavelength at which the half-maximum

¹⁷ R. R. Tucker, Oak Ridge National Laboratory Report No. ORNL-TM-1583, 1966 (unpublished).

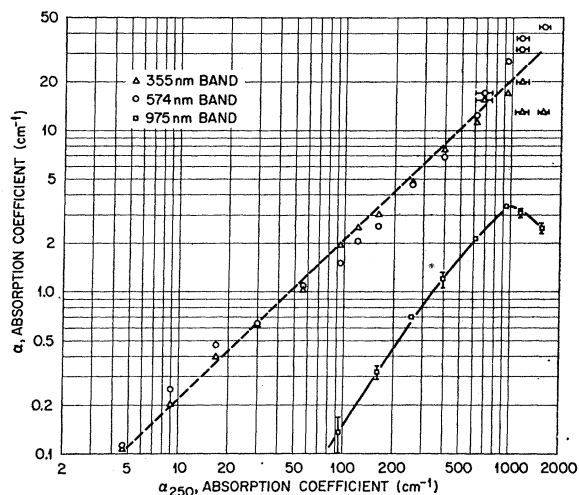


FIG. 2. Absorption coefficients of the bands at 355, 574, and 975 nm versus the absorption coefficient of the 250-nm band for neutron-irradiated crystals.

occurs. Below doses of 6×10^{17} n/cm^2 , this wavelength was found to be independent of dose. Isochronal annealing was accomplished by heating the samples for 10 min at successively higher temperatures in argon atmosphere.

RESULTS

Defect Production

When MgO crystals are irradiated with neutrons at about 60°C , the absorption coefficients of the 250-, 355-, 574-, and 975-nm bands increase with neutron dose. This is illustrated in Fig. 1. The rate of increase of all these bands appears to be similar, although the weak intensity of the 975-nm band at low doses reduces the accuracy. The decrease in absorption of the 355- and 975-nm bands at doses above 3×10^{18} n/cm^2 is quite noticeable. However, subsequent γ irradiation increases the intensity of these bands. This effect is illustrated by the arrows in Fig. 1 for a specimen irradiated to a dose of 5×10^{18} n/cm^2 . After optical bleaching the absorption coefficients of these bands are again reduced to their former values.

In Fig. 2, the logarithm of the absorption coefficient α for the 355-, 574-, and 975-nm bands is plotted against that for the 250-nm band. A straight line with 45° slope is drawn through the experimental points taken from the 355- and 574-nm bands. It appears that there is a direct proportion between the rate of formation of these bands and the F -type 250-nm band and that displacement spikes are responsible for their production.

While the intensities of the 355-, 574-, and 975-nm bands are formed in proportion to that of the F -type defect in neutron-irradiated crystals, only the 250-nm band is observed in additively colored samples or in specimens irradiated with 1.7-MeV electrons. This is shown in Fig. 3. Even though the neutron- and electron-

irradiated crystals have comparable absorption coefficients at 250 nm, these bands are conspicuously absent in the electron-irradiated crystal. When the electron-irradiated sample was rotated so that absorption data were taken through a 7-mm path length, there was still no evidence of any of these three bands. The additively colored sample contained about 1.6×10^{18} F -type defects cm^{-3} (as determined optically from the equation $fn_F = 4.0 \times 10^{18} \alpha_{250}$ with $f=1$ and $\alpha_{250} = 400 \text{ cm}^{-1}$),¹¹ and yet no other bands were observed.

The 355-, 574-, and 975-nm bands, when measured at liquid-nitrogen temperature (LNT), as shown in Fig. 4, exhibit fine structure similar to that reported by other authors.^{3,6,8} The room-temperature (RT) peaks at 355 and 574 nm were observed to shift to 352.5 and 573 nm, respectively, at LNT. The lines at 361.5 and 1044.5 nm have been suggested as zero-phonon lines due to transitions within the same center. The lines at 1004.8 and 967.5 nm were assigned as assisted-phonon lines for the 1044.5-nm zero-phonon line.⁶

Annealing of Defects

The isochronal annealing data of the 250-nm band for five samples, measured at RT, are illustrated in Fig. 5. No significant difference appears between the three neutron-irradiated crystals. The band in the electron-irradiated crystal appears to be somewhat more stable than in the neutron-irradiated samples, and the absorption of the crystal colored with excess Mg exhibits great stability, decreasing to half its original value only at about 1100°C . At various stages during the annealing runs the samples were either γ -irradiated or given a short burst of electrons to ascertain that the

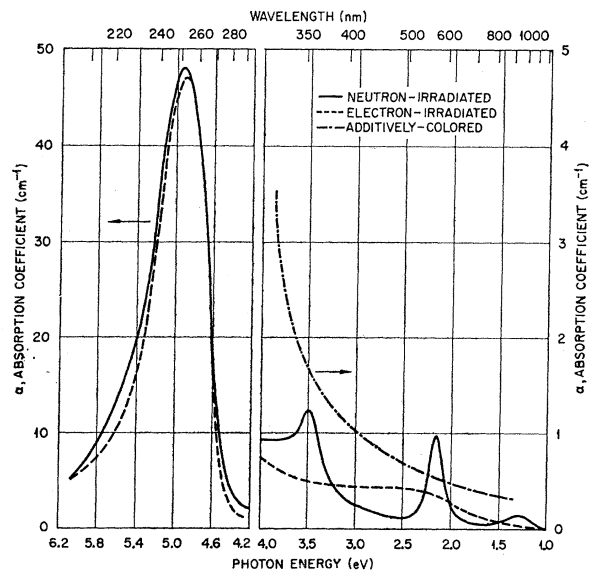


FIG. 3. Comparison of the spectra of crystals produced by electron irradiation, neutron irradiation, and additive coloration. The 250-nm band for the additively colored crystal ($\alpha_{250} = 400 \text{ cm}^{-1}$) is not shown here.

changes were not due to thermal redistribution of charge on the defects. In all these crystals, the effect of annealing was monitored by ESR as well as optical methods and there was good agreement between the measurements.

The annealing data for the two zero-phonon lines at 361.5 and 1044.5 nm, and the absorption bands at 250, 352.5, 573, and 975 nm in a neutron-irradiated crystal, are plotted in Fig. 6. There is a similarity in the annealing of the zero-phonon lines¹⁴ and in the annealing of the 353- and 975-nm bands. However, there is no similarity between the annealing of the absorption coefficients of the zero-phonon lines and those of the two broad absorption bands. It was observed that the half-widths of the zero-phonon lines decreased by about a factor of 2 during the annealing treatments. Thus it is impossible to state that the lines are not associated with the bands. In the same figure, the 573-nm band annealed out at approximately the same rate as the 250-nm band, up until 325°C. At this temperature, a band at 565 nm begins to appear, and increases with temperature to about 500°C. The 573- and 565-nm bands are plotted as one curve in the figure.

We attempted to produce the *M*-like and *R*-like zero-phonon lines, observed in neutron-irradiated MgO, in heavily electron-irradiated and additively colored crystals. In the case of 1.7-MeV electron irradiation, the absorption coefficient of the 250-nm band, α_{250} , saturated at $\sim 90 \text{ cm}^{-1}$ for an irradiation temperature of $\sim 50^\circ\text{C}$ and actually decreased to about 65 cm^{-1} after a dose of about 10^{20} e/cm^2 . The *F*-center growth also appeared to saturate even when samples were irradiated at -170°C . No zero-phonon lines were observed in either the electron-irradiated crystals or the additively colored specimen even though the latter had an initial $\alpha_{250} = 400 \text{ cm}^{-1}$. Moreover, no new defects were detected during annealing of an electron-irradiated crystal of $\alpha_{250} = 47 \text{ cm}^{-1}$ or of the additively colored sample. However, when additively colored, electron-irradiated or neutron-irradiated crystals were

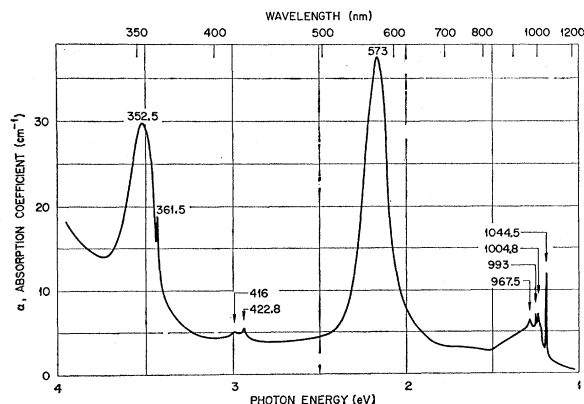


FIG. 4. Absorption spectrum of a crystal, measured at LNT, produced by an irradiation of 2.2×10^{18} neutrons/cm².

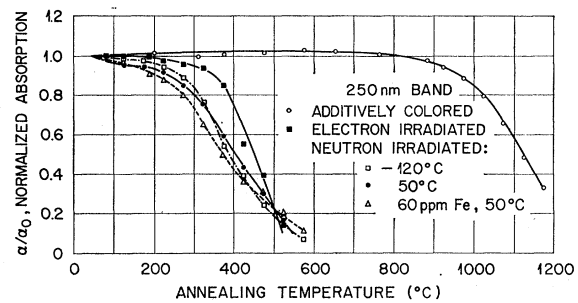


FIG. 5. Normalized absorption coefficient α/α_0 of the 250-nm band versus annealing temperature for electron-irradiated, neutron-irradiated, and additively colored crystals.

either γ - or electron-irradiated (10^{25} e/cm^2) after annealing at temperatures above 900°C , new structures were observed. The optical spectrum of the additively colored crystal after annealing at 1240°C and subsequent irradiation is shown in Fig. 7. Zero-phonon lines at 1324.2 and 1081.6 nm are visible.

Since the additively colored sample was cooled rapidly from 1740°C after being exposed to Mg vapor, a check was made to find out whether the spectra shown in Fig. 7 were of thermal origin. An as-received crystal was oil-quenched from 1770°C , annealed at 1240°C for 10 min, and then γ -irradiated. Even though this treatment was very similar to that received by the additively colored sample, the lines shown in Fig. 7 were not present. This indicates that negative-ion vacancies introduced by the Mg vapor are primarily responsible for this absorption.

DISCUSSION AND SUMMARY

In a cubic lattice it is possible to form *M* centers by low-temperature irradiation or by additive coloration simply because statistically there is a certain probability that two negative-ion vacancies will be formed on adjacent lattice sites, e.g., $M = (6/N_0)F^2$, where N_0 is the number of negative-ion lattice sites and M and F are the concentrations of *M* centers and *F* centers, respectively. A similar argument shows that the concentration of *R* centers should be proportional to the cube of the *F*-center concentration. An analysis of the *F*-center concentrations in our electron-irradiated samples indicates that we have far too few *F*-type centers to expect to see aggregate centers. In the additively colored sample, on the other hand, there are sufficient *F* centers present such that one might expect *M* centers to be detectable experimentally; yet we do not see in this sample either the broad bands at 355, 574, and 975 nm or the zero-phonon lines attributed to *M*- and *R*-like centers.

Thermal annealing of irradiated and additively colored crystals produced some very interesting results. It is clear from the data presented in Fig. 5 that negative-ion vacancy motion does not occur until at least 900°C , and that the annealing of the 250-nm band

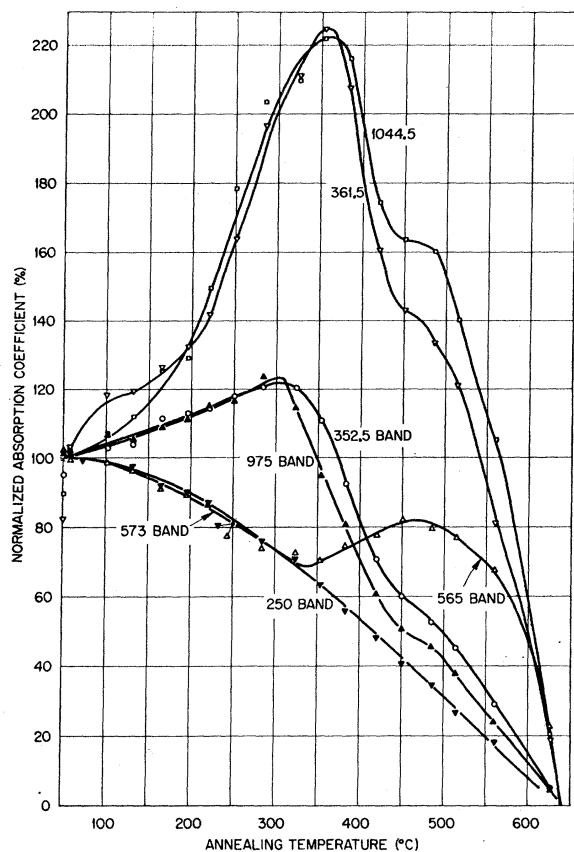


FIG. 6. Normalized absorption coefficients α/α_0 of the bands and two zero-phonon lines in crystal irradiated with 2.2×10^{18} neutrons/cm² versus annealing temperature. The initial absorption coefficients for the 250-, 352.5-, 573-, and 975-nm bands are 920, 22, 34, and 4 cm⁻¹, respectively, and those for the zero-phonon lines at 361.5 and 1044.5 nm are 6 and 10 cm⁻¹, respectively.

at lower temperatures in the irradiated crystals is probably due to interstitial-vacancy recombination.

The zero-phonon lines at 1081.6 and 1324.2 nm which appear in the additively colored crystals with heat treatment can also be induced in neutron- and electron-irradiated crystals by annealing above 900°C. Moreover, it has been shown¹⁸ that these same two zero-phonon lines appear in deformed crystals which have been annealed at high temperature and either γ - or electron-irradiated. That these two zero-phonon lines are not due to transitions from the same center is clear from the annealing data. After annealing at 958°C the line at 1324.2 nm is much larger than that at 1081.6 nm, but after annealing at 1210°C the reverse is true. The fact that the temperature at which the zero-phonon lines appear in electron-irradiated, neutron-irradiated,

¹⁸ W. A. Sibley, J. L. Kolopus, and W. C. Mallard, *Phys. Status Solidi* **31**, 223 (1969).

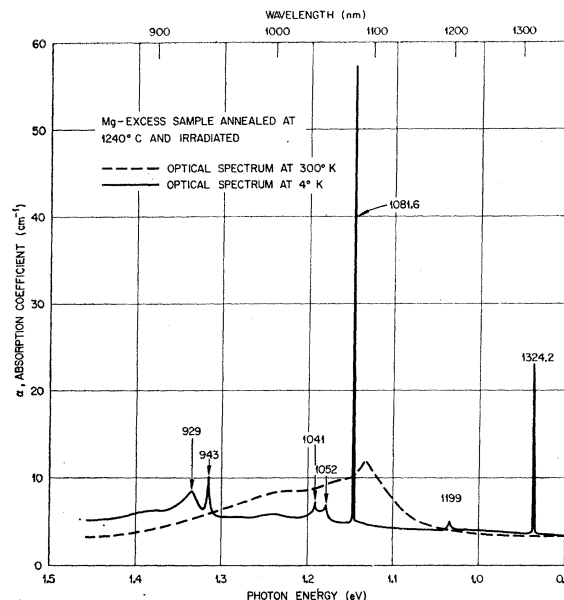


FIG. 7. Absorption spectra at room and liquid-helium temperatures of an additively colored crystal after annealing at 1240°C and a short electron irradiation at LNT.

deformed, and additively colored crystals coincides with the temperature at which negative-ion vacancies begin to disappear suggests that they are due to F -aggregate centers. On the other hand, there is the possibility that these zero-phonon lines are due to clusters involving positive- and negative-ion vacancies.

In summary we would like to reiterate the following points.

- (1) The defects which are responsible for the 355-, 574-, and 975-nm absorption bands in neutron-irradiated crystals are apparently formed in displacement spikes created by the high-energy neutrons since they are produced linearly with the F -type centers.
- (2) The difference in annealing behavior of the F -type centers in additively colored and irradiated specimens suggests that interstitials are the mobile entity in the irradiated crystals and that the F -type centers are not mobile below 900°C.
- (3) The observation that the 1081.6- and 1324.2-nm zero-phonon lines can be created in all the crystals studied and that they appear only after negative-ion vacancies anneal out suggests to us that they are due to F -aggregate centers.

ACKNOWLEDGMENTS

We would like to thank J. L. Kolopus for the ESR measurements during the course of this work and Brian Henderson for his helpful suggestions and comments.