

# ABSORPTION BANDS WITH ZERO-PHONON LINES IN NEUTRON-IRRADIATED MgO CRYSTALS

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## SYNOPSIS

The optical absorption of "pure" and Co-, Ni-, and Cr-doped MgO crystals irradiated by reactor neutrons are studied in the temperature range from 300°K to LHeT.

Irradiation-induced 352 and 980 nm bands appear in doped crystals as well as in "pure" one. The 352 nm band is enhanced by the presence of Cr-ion impurities, while the 980 nm band is independent on impurities.

It is suggested that the 352 nm band is due to Cr-associated center, and the 980 nm band to intrinsic color center, possibly, the  $M^-$  center.

Both the 352 and 980 nm bands are accompanied with the zero-phonon lines at 361 and 1044 nm, characteristics of which are investigated as functions of the temperature. The results can be well described by using the effective Debye temperatures.

## § 1 Introduction

Nowadays, color centers in ionic crystals composed of divalent constituents are one of the most attractive problem in solid state spectroscopy, since the color center studies on alkali-halides have been almost established. However, the color center studies on such divalent crystals are not easy for lack of the single crystal of high purity.

Since MgO is of the same crystal structure as the fcc alkali-halides and its single crystal is available commercially, interpretations for the absorption bands due to defect centers in MgO have been attempted more frequently than in other crystals, referring the results on color center in alkali-halides.<sup>1-5)</sup>

The MgO crystals have more possibility for new defect centers than alkali-halides, because the constituent ions are divalent and the so called "pure" (undoped) single crystal contains various transition metal ions as inevitable impurities.\* Thus, it is quite important to ascribe irradiation-induced absorptions in the "pure" crystals to either intrinsic defect centers or impurity-associated centers.

In most cases, color centers were introduced in MgO crystals by the neutron

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\* Recently, Henderson and Wertz [see, reference (7)] have proposed a systematic notation for color centers in divalent ionic crystals using the same capital letters as in the alkali-halides with superscripts added to indicate the charge state of the center in order to avoid the confusion arising from the number of trapped electrons in the center. According to this notation, for instance, a negative ion vacancy with single trapped electron is designated as  $F^+$  center and a negative ion vacancy with two trapped electrons is designated as  $F$  center.

irradiation. Many absorption bands were observed in neutron-irradiated crystals by Clarke<sup>6)</sup> firstly, in the wavelength region from 200 to 1200 nm. Among these absorption bands, the 245 nm band has been ascribed to the F<sup>+</sup> center (single negative ion vacancy with one trapped electron) by Wertz et al.,<sup>7,8)</sup> by Kemp and Neeley,<sup>9)</sup> by Henderson and King<sup>10)</sup> and by Kemp et al.<sup>11)</sup> The 288 nm band was ascribed to Fe<sup>3+</sup> ion center by Soshea et al.<sup>12)</sup> and by Hansler and Segelken.<sup>13)</sup> The broad band at 572 nm was assigned to F band by Wertz et al.<sup>8)</sup>

As for the identifications of the absorption bands at 352 and 980 nm, both being accompanied with zero-phonon lines, there have been still remaining some ambiguities. Present author suggested previously<sup>5)</sup> that the 352 nm band is due to Cr-associated center and the 980 nm band to intrinsic defect center, probably M-center. However, Ludlow<sup>14)</sup> and Henderson and Wertz<sup>7)</sup> have the opinion that the 352 and 980 nm bands are due to same intrinsic defect center. Under these circumstances it is necessary to refine the previous work<sup>5)</sup> and to give the clear identification of the bands under discussions.

In the present work, the influence of transition metal impurities on both 352 and 980 nm bands are investigated more precisely, and a comparison with the color center absorptions in alkali-halides is made with the aid of the zero-phonon line associated with 980 nm band. In addition to these, the temperature dependences of the characteristics of zero-phonon lines associated with both 352 and 980 nm bands are discussed.

## § 2 Experimental

The "pure" (undoped) MgO crystals were purchased from Semi-Elements Company. The following impurities were spectroscopically detected in weight per cent; Fe(0.01), Mn(0.003), Si(0.01), Cr(0.003), Ba(0.0003), Ca(0.01) and B(0.008). Crystals were cleaved to be a plate of about  $10 \times 10 \times 0.7$  mm<sup>3</sup> for absorption measurements and were not polished usually. As-received crystals exhibited a strong *uv* absorption due to the Fe<sup>3+</sup> ion, i.e. absorption for photon energies larger than 4 eV. Since this absorption was found to bleach thermally, all specimens used for neutron irradiations were subjected heat treatments in order to reduce the strong *uv* absorption down to 0.1 or less in optical density at 6.0 eV.

The doped crystals were also from Semi-Elements Company. These are as follows:

MgO	doped	with	0.05	mole%	of	Cr <sub>2</sub> O <sub>3</sub>
"	"	"	1	"	"	Co
"	"	"	1	"	"	NiO

Doped specimens also showed the strong *uv* absorption due to Fe<sup>3+</sup> ions in the region above 4eV.

In order to introduce color centers in specimens, neutron irradiations were made either in LNTL\* (Liquid Nitrogen Temperature Loop) of the Japan Research Reactor 2 or in Hydraulic Tube\*\* of the KUR(Kyoto University Reactor). The specimens were exposed to prolonged neutron irradiation up to a dose of  $10^{18} \sim 10^{19}$

\* Average thermal neutron flux in this facilities;  $2 \times 10^{13}$  neutrons/cm<sup>2</sup>/sec. Cadmium ratio of Au foil; 27.8. Irradiations were made at 80°K.

\*\* Average thermal neutron flux;  $2.2 \times 10^{13}$  neutrons/cm<sup>2</sup>/sec. Cadmium ratio of Au foil; 4.0. Irradiations were made at 320°K.

nvt (total). In both cases, specimens were also wrapped in aluminum foils. Specimens irradiated in LNTL were stored in liquid nitrogen before optical measurements.

The absorption measurements in most cases were carried out using a Hitachi recording spectrophotometer (EPS-3) in the temperature range from RT(room temperature) to LNT(liquid nitrogen temperature) with a conventional cryostat. For high resolution measurements on the zero-phonon lines in the temperature range from RT to LHeT(liquid helium temperature), a Cary Model 14 spectrophotometer was used at the slowest scanning speed. Resolutions of the measurements at 1000 nm in this case were about 0.3 nm.

When the specimens irradiated in LNTL are transferred to the metal cryostat for absorption measurement, it was inevitable for specimens to raise their temperature for a short period. Irradiated specimens were mounted on the sample holder of the cryostat in the dark. The temperature of the specimen was measured by an Allen-Bradley carbon resistor or by a copper-constantan thermocouples.

### § 3 Results

In most "pure" crystals as-received, there is an intense absorption band at 288 nm, and the tail of this absorption gives rise to visible yellowish color for thick crystals. The 288 nm absorption band which had been regarded as absorption band due to  $Fe^{3+}$  ion<sup>12)</sup> was bleached by heating in vacuum above 1150°C without serious damage on the surface. The annealing effect for a specimen of 0.5 mm thick is shown in Fig. 1. It was required about 12 hours for a specimen of 0.5 mm thick to reduce  $uv$  absorption down to 0.1 or less in optical density below 5.0eV.

Absorption spectra of the neutron-irradiated "pure" MgO crystals in the visible

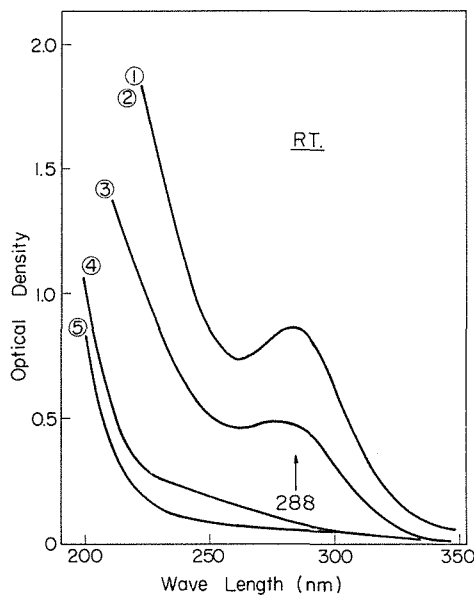


Fig. 1. Annealing effect on absorption spectra of MgO single crystals. ①: as received, ②: annealed for 4 hours at 1000°C, ③: ② plus 2 hours at 1150°C, ④: ③ plus 2 hours at 1200°C, ⑤: annealed for 12 hours at 1200°C. Measurements were carried out at RT (room temperature).

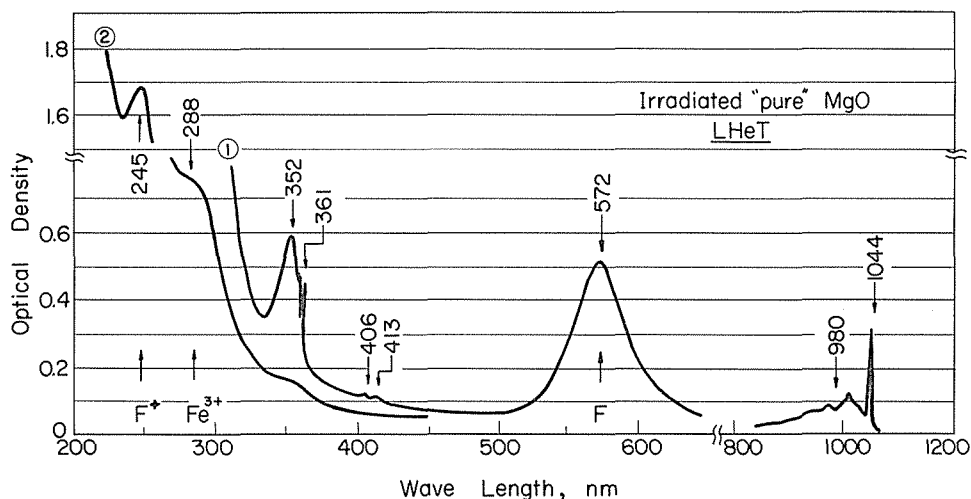


Fig. 2. Absorption spectra at LHeT (liquid helium temperature) of "pure" MgO crystal irradiated with neutrons in the Liquid Nitrogen Temperature Loop. (1): irradiated at LNT to a dose of  $8 \times 10^{18}$  nvt, (2): irradiated at LNT to a dose of  $1.2 \times 10^{18}$  nvt.

and  $uv$  regions measured at LHeT are shown in Fig. 2. As seen in the figure, the irradiated specimen showed five remarkable absorption bands at 245, 288, 352, 572 and 980 nm, two of which were accompanied with the sharp lines on the longer wavelength tails. Weak absorption pips were also appreciable at 406 and 413 nm. The band at 245 nm is probably due to  $F^+$  center<sup>8-11)</sup> (negative ion vacancy with one trapped electron) and the band at 572 nm has been assigned to  $F$  band<sup>9)</sup> (single negative ion vacancy with two trapped electrons). The band at 288 nm due to  $Fe^{3+}$  ion was recovered by neutron irradiation. The bands at 352 and 980 nm accompanied sharp lines at 361 and 1044 nm, respectively, which have been assigned as the zero-phonon lines.<sup>8,14-19)</sup> These two bands are the main interests in this work.

With the purpose to investigate the role of the impurities, doped specimens were irradiated and their absorption spectra were compared with that of "pure" one. In Fig. 3 are shown the absorption spectra of the irradiated  $MgO:Co^{2+}$ ,  $MgO:Ni^{2+}$ , and  $MgO:Cr^{3+}$  measured at RT and LNT (Valence states of the impurity ions in  $MgO$  were discussed thoroughly by Low<sup>20)</sup>).

As shown in the figure, spectra of any doped specimen shows the common bands at 352, 572 and 980 nm. Extra bands at 400 and 460 nm, and small hump at about 680 nm were observed for Ni-doped specimen (Fig. 3-b). Spectra of Co-, and Cr-doped specimens are practically the same as that of "pure" one. It is noticeable, however, that the irradiation-induced 352 nm band in Cr-doped specimen is much enhanced than the same bands in the other crystals. The intensity of every band in all specimens (except 400 nm band in Ni-doped specimen) grow higher with increasing irradiation dose.

Absorption spectra of Co-, and Cr-doped specimens at LNT were practically the same as that of "pure" one, except small pips near 420 nm (Figs. 3-d and 3-f), while 370 nm band in the absorption spectra of Ni-doped specimens was resolved

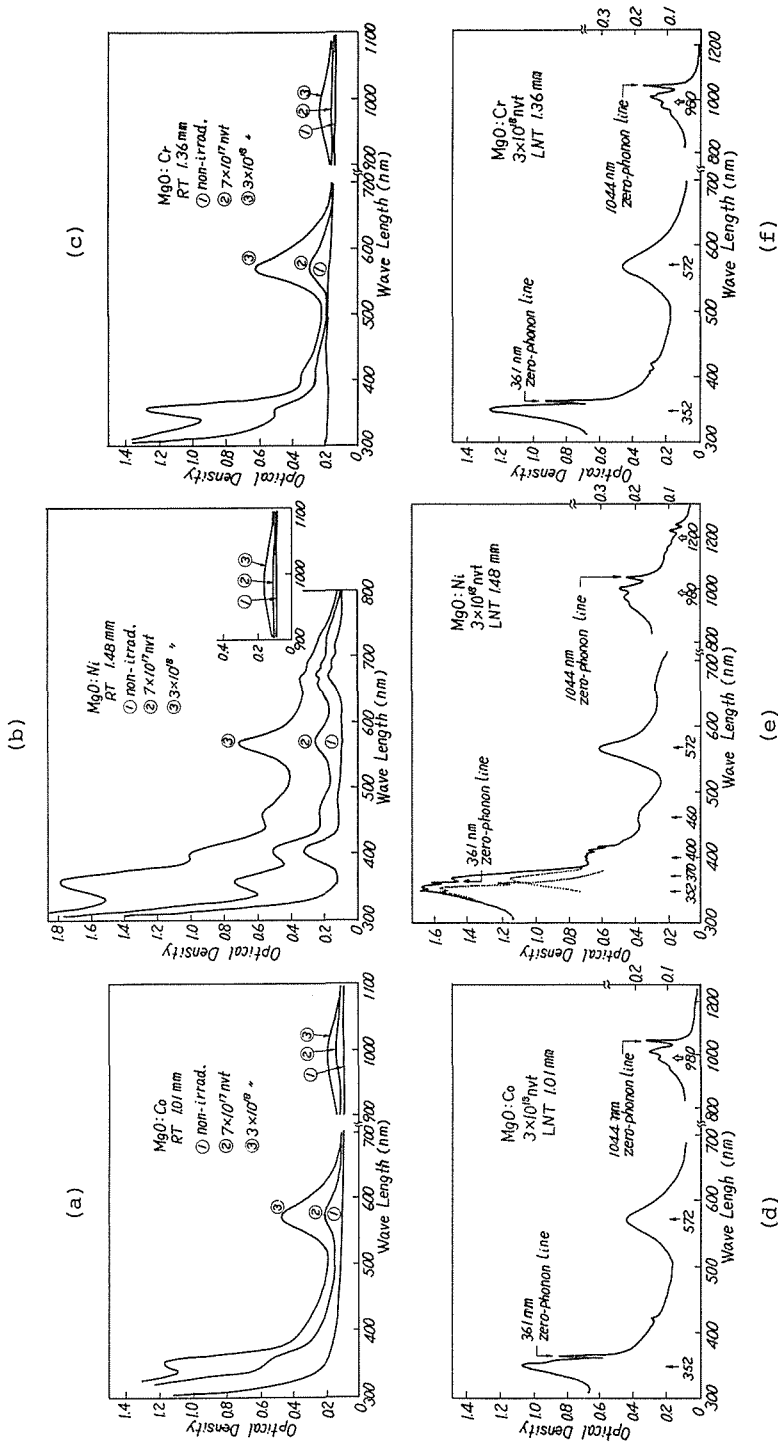


Fig. 3. Irradiation-induced absorption spectra of Co-, Ni-, and Cr-doped crystals. Temperature of sample during irradiation was 320°K, measurements were carried out at RT (Figs. 3-a, 3-b, 3-c), and at LNT (Figs. 3-d, 3-e and 3-f).

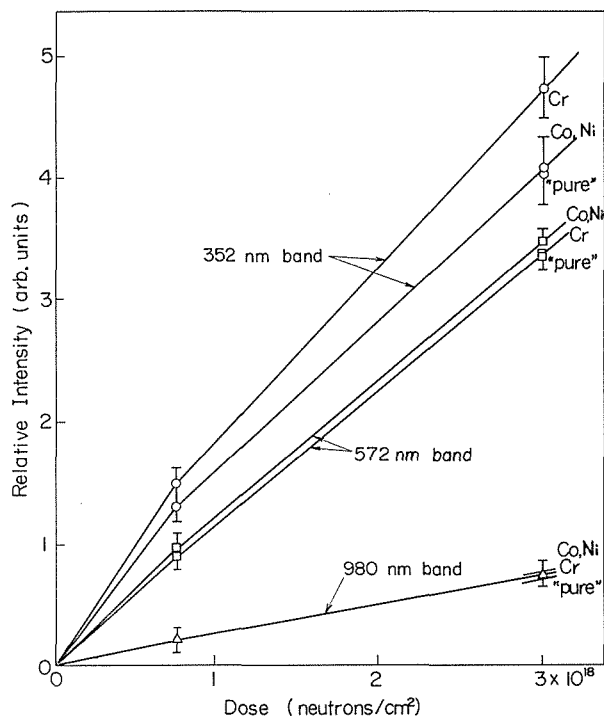


Fig. 4. Growth curves of the 352 (—○—), 572, (—□—), and 980 (—△—) nm bands of the "pure", Co-, Ni-, and Cr-doped crystals irradiated in Hydraulic Tube. Measurements were carried out at LNT.

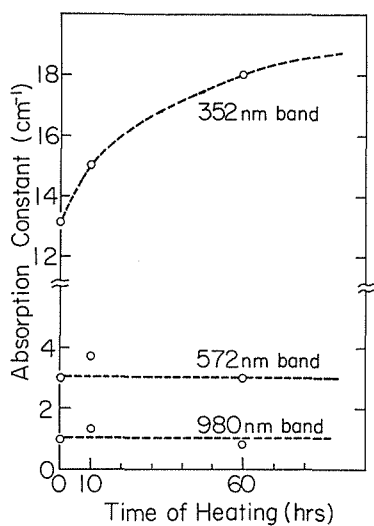


Fig. 5. Influence of  $\text{Cr}_2\text{O}_3$ -roasting treatments on the 352, 572 and 980 nm absorption band intensities. Samples were irradiated by neutrons of about  $2 \times 10^{18}$  nvt in Hydraulic Tube after the treatments.

from 352 nm band at LNT (Fig. 3-e). Sharp lines accompanied to 352 and 980 nm bands became appreciable at LNT for any doped specimen. Extra sharp lines appeared on the longer wavelength tail of the 400 nm band and near 1200 nm band at LNT for Ni-doped specimen.

Dose dependence of the intensities of absorption bands at 352, 572 and 980 nm, common to "pure" and doped specimens, are shown in Fig. 4. As seen in the figure, 980 and 572 nm bands, which increased almost linearly with irradiation dose up to about  $10^{19}$  nvt for "pure" specimens<sup>5)</sup>, were independent of impurities. While, 352 nm band was enhanced for Cr-doped specimens.

Influence of the presence of Cr-ion on the 352 nm band is shown in Fig. 5. "Pure" specimen coated by  $\text{Cr}_2\text{O}_3$  powder was heated in vacuum at 1300°C for 10 or 60 hours. With this treatment, one can obtain a thin layer near the surface of the crystal where the concentration of Cr-ion is fairly high. After this treatment, specimen was irradiated with neutrons of about  $2 \times 10^{18}$  nvt in Hydraulic Tube. Absorption constants of the 352, 572 and 980 nm bands at RT for specimens treated as described above are plotted against the time of heating in Fig. 5. The figure shows that the intensity of 352 nm band is increased with heating time, whereas 572 and 980 nm bands are not affected by such heat treatments.

#### § 4 Discussions on the 352 and 980 nm bands

Among the three absorption bands at 352, 572, and 980 nm common to "pure" and doped crystals, the 572 nm band has been ascribed to F center.<sup>8)</sup> While, the origin of the 352 and 980 nm bands accompanying sharp zero-phonon lines have not been established yet, though many workers discussed these bands.<sup>5,7,8,14,15,21)</sup> Ludlow<sup>14)</sup> and Henderson and Wertz<sup>7)</sup> argue that the 352 nm band is due to intrinsic lattice defects and not to impurity centers. However, results of our previous work<sup>5)</sup> suggest that this band may not be intrinsic. The author's main interest on these bands in this paper is whether their origin is due to intrinsic lattice defects or impurity associated centers. As shown in the Figs. 2 and 3, the 352 and 980 nm bands are observed for both "pure" and doped crystals. The intensities of irradiation-induced 980 nm band are almost same for "pure" and doped crystals, while the 352 nm band is more enhanced for Cr-doped crystal than other ones. This difference is clear in growth curves of 352, 572 and 980 nm bands of "pure" and doped crystals at LNT, as shown in Fig. 4.

From the Fig. 4, one can conclude that both 572 and 980 nm bands are independent of impurities (as far as Cr, Ni, and Co are concerned) while the 352 nm band is closely connected with Cr-ion impurities. The results shown in Fig. 5 means that the presence of Cr-impurities contribute to the 352 nm band unambiguously and this supports the above conclusion.

Here, one may be interested in the question of whether the 352 nm band is independent of the valence changes of the Cr-ion impurities or not. Of the impurity ions observed in MgO, those of Co-, Ni-, and Cr-ion are readily converted to different valence states. But, it is usual that the Cr-ion exists preferentially in the trivalent state, though the divalent state results temporarily on irradiation.<sup>22)</sup>

As stated above, the 980 nm band seems independent of impurities, so it is probably due to intrinsic center. As mentioned in § 1, it is quite useful to refer the characteristics of intrinsic color centers in alkali-halides to make assignments of intrinsic color centers in MgO crystals, because the MgO has the same crystal

structure as alkali-halides.

It is well known that if the position of color center bands are plotted for each fcc alkali-halide as a function of lattice constant, the definite smooth curve results for each color center (the Mollwo-Ivey plot). Fitchen, Fetterman and Pierce<sup>23)</sup> gave such a plot for the *zero-phonon lines* associated with the negatively charged  $M^-$  and  $R^-$  centers (in which an extra electron is trapped at M or R center) for several fcc alkali-halides. Their plots are shown in Fig. 6.

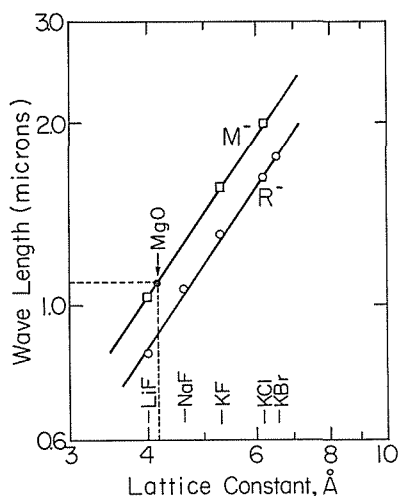


Fig. 6. The Mollwo-Ivey plot of absorption wavelength of zero-phonon lines at 4°K vs lattice constant [c.f. Fig. 3 of reference (23)].

Putting lattice constant of MgO (4.2 Å) on the figure, the values of 1.1 and 0.9 microns are predicted for the absorption peak of zero-phonon lines of the  $M^-$  and  $R^-$  centers in MgO, respectively. The experimental value (1.044 microns) for the zero-phonon line associated with 980 nm band is very close to 1.1 micron. Therefore, it is possible to assign tentatively the 980 nm band in MgO to the  $M^-$  band ( $M^-$  center with five electrons). Similer relation has been recognized of F-bands in LiF and MgO crystals; namely the positions of F bands in both crystals are very close to each other (243 nm and 245 nm at LHeT) and the lattice constants are 4.0 and 4.2 Å for LiF and MgO, respectively.

## § 5 Discussions on zero-phonon lines

### 5.1 Zero-phonon lines in MgO

As mentioned in § 3, (Figs. 2, 3-d, 3-e, and 3-f) sharp absorption lines at 361 and 1044 nm were observed on the lower energy side of broad bands at 352 and 980 nm, respectively. These sharp lines are interpreted as optical transitions in which no energies are transferred to the lattice phonons and hence are called zero-phonon lines.<sup>24-31)</sup> The zero-phonon lines of the MgO crystal at 361 and 1044 nm were first reported by Wertz et al.<sup>22)</sup> and further experiments have been developed by several authors.<sup>5,7,8,14,15,21)</sup> As described in previous section, the zero-phonon line at 1044 nm associated with 980 nm band play an important role for assignment of the band.



In this paragraph, we mainly concern ourselves with the characteristics of the zero-phonon lines in neutron-irradiated MgO crystals. Same crystals mentioned in § 2 were used for zero-phonon line study.

In Figs. 7 and 8, are shown the profile of the 980 and 352 nm bands measured at LHeT. Sharp line at 1044 nm in Fig. 7 is assigned to zero-phonon line and other structure are considered to be phonon-assisted absorption lines.\* Similarly, the

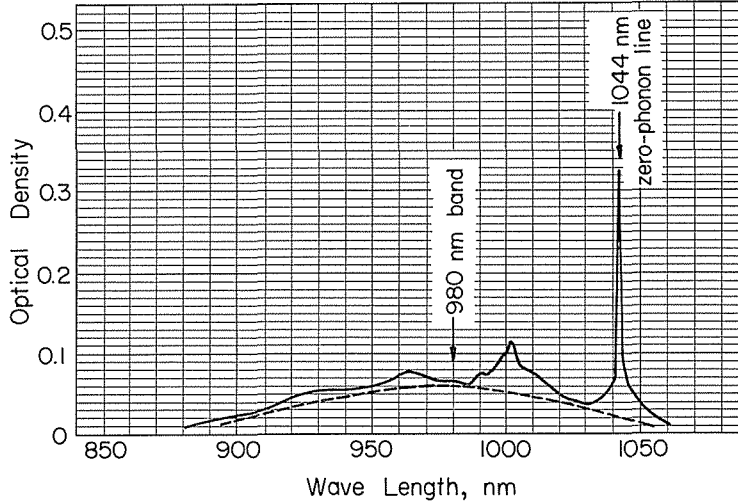


Fig. 7. Absorption spectrum of the 980 nm band, showing details of zero-phonon line and phonon-assisted fine structure at LHeT.

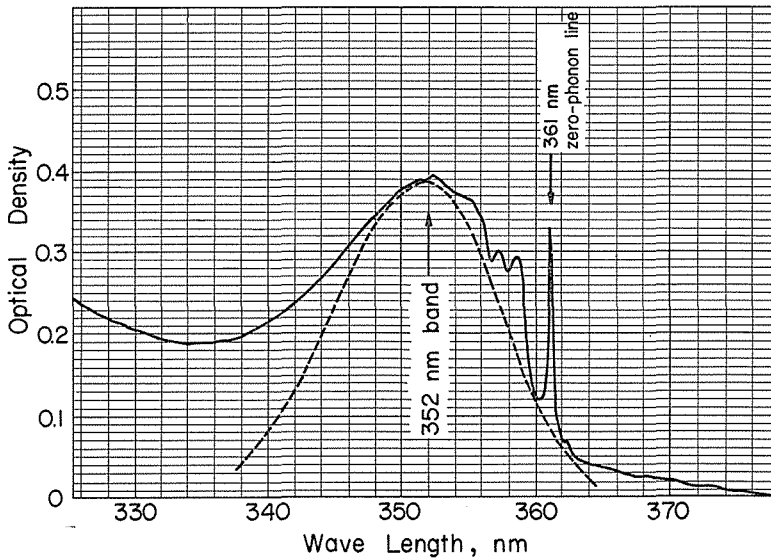


Fig. 8. Absorption spectrum of the 352 nm band, showing details of zero-phonon line and phonon-assisted fine structure at LHeT.

\* Similar spectra shown in Fig. 3-d, 3-e, and 3-f were measured at LNT, while the spectrum in this figure was measured at LHeT to get precise fine structure and shown in expanded wavelength scale.

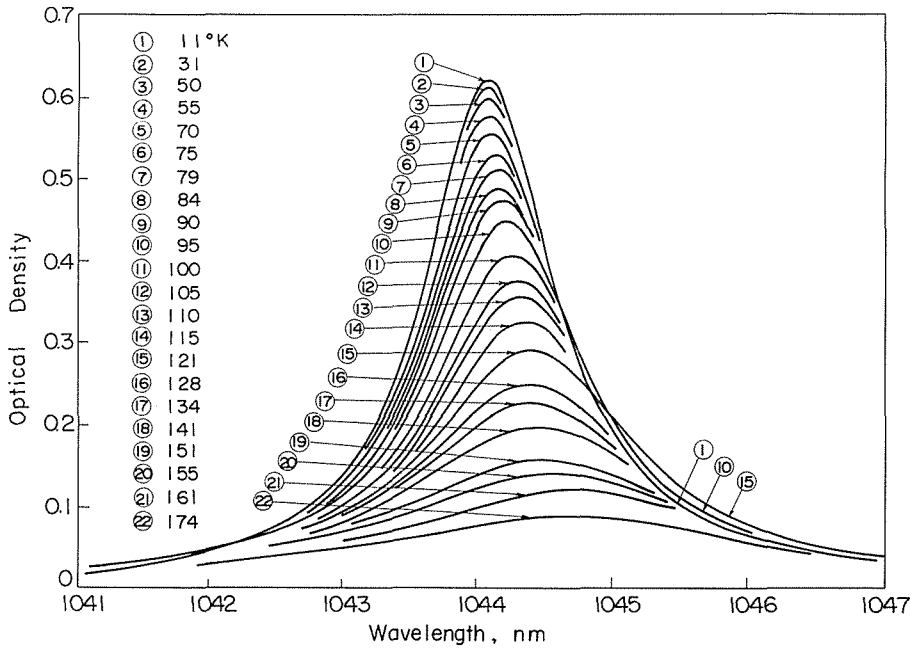


Fig. 9. Temperature dependence of the 1044 nm line.

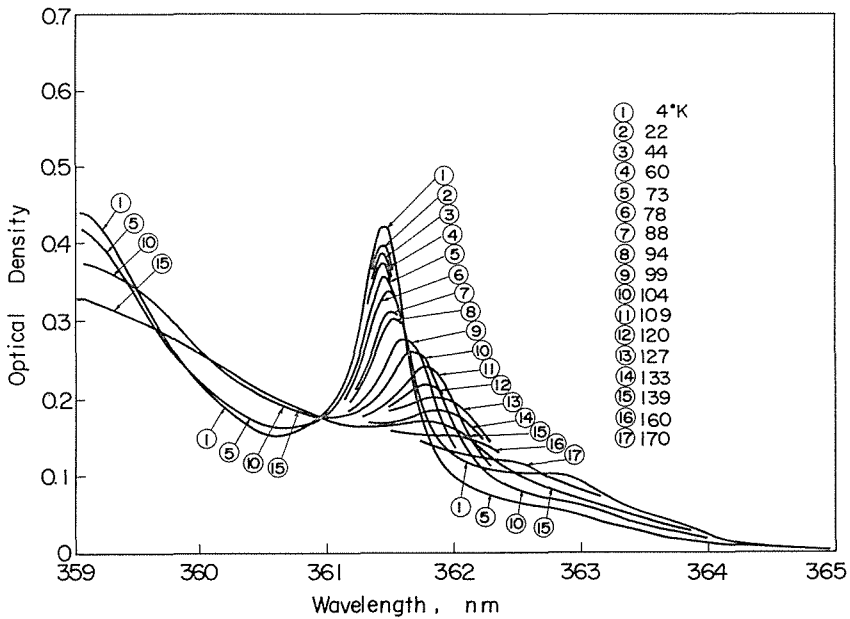


Fig. 10. Temperature dependence of the 361 nm line.

sharp line at 361 nm in Fig. 8 is also assigned to zero-phonon line and other peaks are considered to be phonon-assisted absorption lines. Dotted curves in both figures show the broad bands at 980 and 352 nm, respectively.

The temperature dependence of the zero-phonon lines are shown in Figs. 9 and 10. As seen in the figures the intensities of the absorption lines decrease rapidly, the peaks shift towards lower energy, and the half-widths of the lines become broader with increasing temperature.

5.2 *Relative intensity*

Intensity ratio of the zero-phonon line at 361 nm to broad band at 352 nm is plotted against the temperature in Fig. 11. Experimental points can be fitted well to the following equation;

$$I_s/I_b = \exp[-S\{1+6.6(T/\theta_D)^2\}] \text{ for } T \ll \theta_D \tag{1}$$

which comes from Debye-Waller factor using Debye approximation.<sup>24,32,33</sup> In Eq. (1),  $I_s$  and  $I_b$  are the integrated intensities of the sharp line and the broad band, respectively,  $\theta_D$  is the effective Debye temperature and  $S$  denotes the most probable number of phonons involved in the transition (Huang-Rhys factor). The values  $S$  obtained from the curve in Fig. 11 is 4.0. The effective Debye temperature  $\theta_D$  determined from the curve is 652°K. This value is somewhat lower than the Debye temperature 760°K determined from specific heat measurements of crystalline MgO (at about 100°K).<sup>34</sup> Similar analysis was done roughly for the 1044 nm line and obtained  $S \sim 2$  and  $\theta_D = 800 \pm 100$ °K.

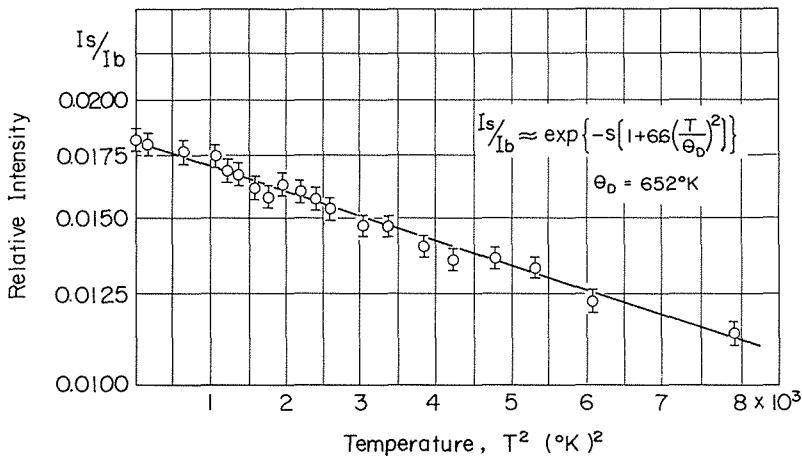


Fig. 11. Temperature dependence of the ratio of the integrated absorption intensity of zero-phonon line to that of the 352 nm band.

The  $S$  values obtained here indicate that the strength of the electron-lattice coupling of the centers is fairly weak compared with that of F centers in alkali-halides ( $S \sim 20$ ). Discrepancy between the effective Debye temperatures and bulk Debye temperature probably reflects the fact that constituents of the centers under consideration have different effective masses from those of host ions.<sup>35</sup>

5.3 *Peak shift*

In Fig. 12 peak shift of the zero-phonon lines are plotted against the temperature.

Experimental points can be fitted fairly well to the theoretical curve derived by McCumber and Sturge,<sup>35)</sup>

$$E(0) - E(T) = \alpha(T/\theta_D)^4 \int_0^{\theta_D} dt \frac{t^3}{e^t - 1}, \quad (2)$$

where  $\theta_D$  is the effective Debye temperature,  $\alpha$  is taken as an adjustable parameter for strength of the quadratic electron-lattice coupling.  $E(T)$  and  $E(0)$  are the peak positions at  $T^\circ\text{K}$  and  $0^\circ\text{K}$ , respectively.\*

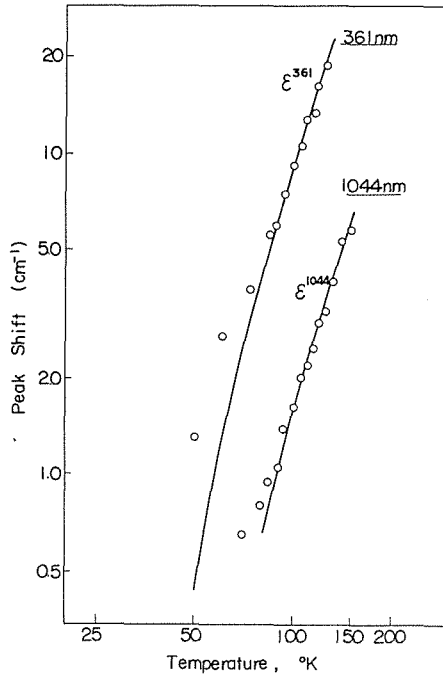


Fig. 12. Temperature dependence of the peak shift of the zero-phonon lines at 1044 and 361 nm. The theoretical curves were derived from Eq. (2) with  $\theta_D = 800 \pm 5^\circ\text{K}$  and  $\alpha = 4.6 \times 10^2 \text{ cm}^{-1}$  for 1044 nm line and  $\theta_D = 652^\circ\text{K}$  and  $\alpha = 2.7 \times 10^3 \text{ cm}^{-1}$  for 361 nm line.

As seen in Fig. 12, one can get the theoretical curves well fitted to experimental points except in the lower temperature region by using  $\theta_D = 800 \pm 5^\circ\text{K}$ , for 1044 nm line and  $\theta_D = 652^\circ\text{K}$  for 361 nm line, which are obtained from the intensity ratio analysis. For these  $\theta_D$ s,  $\alpha = 4.6 \times 10^2 \text{ cm}^{-1}$  for 1044 nm line and  $\alpha = 2.7 \times 10^3 \text{ cm}^{-1}$  for 361 nm line were obtained.

#### 5.4 Line broadening

Temperature dependence of the half-widths of the zero-phonon lines are shown in Fig. 13. Experimental points are fitted well to the following equation;

$$\Gamma(T) = \Gamma(0) + \beta(T/\theta_D)^7 \int_0^{\theta_D} dt \frac{t^6 e^t}{(e^t - 1)^2}, \quad (3)$$

\* Mention should be made here of the error in Eq. (2) of the paper appearing in J. Phys. Soc. Japan **24** (1968) 96. The right side of Eq. (2) should read  $E(0) - E(T)$ .

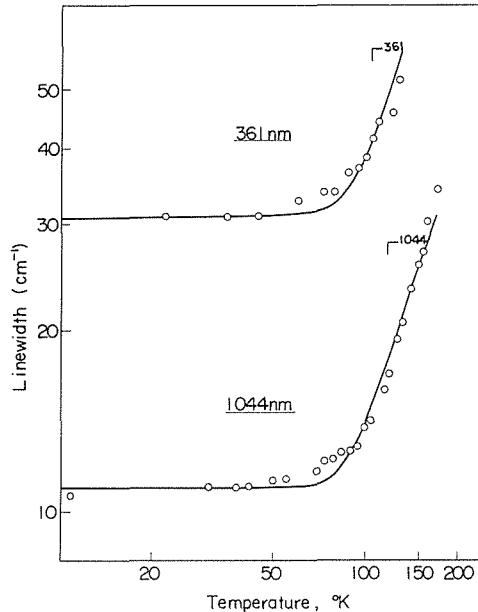


Fig. 13. Temperature dependence of the half-width of the zero-phonon lines. The theoretical curves were derived from Eq. (3) with  $\theta_D=800^\circ\text{K}$ ,  $\beta=1.1 \times 10^4 \text{ cm}^{-1}$  and  $\Gamma(0)=11.0 \text{ cm}^{-1}$  for 1044 nm line, and  $\theta_D=652^\circ\text{K}$ ,  $\beta=1.6 \times 10^4 \text{ cm}^{-1}$  and  $\Gamma(0)=31.0 \text{ cm}^{-1}$  for 361 nm line.

which is derived by McCumber and Sturge,<sup>35)</sup> where  $\beta$  is also adjustable parameter like  $\alpha$ . Similarly in the preceding section,  $\theta_D=800^\circ\text{K}$  for 1044 nm line and  $652^\circ\text{K}$  for 361 nm line give the theoretical curve well fitted to experimental points as seen in Fig. 13. In these case we have put  $\beta=1.1 \times 10^4 \text{ cm}^{-1}$  and  $\Gamma(0)=11.0 \text{ cm}^{-1}$  for 1044 nm line, and  $\beta=1.6 \times 10^4 \text{ cm}^{-1}$  and  $\Gamma(0)=31.0 \text{ cm}^{-1}$  for 361 nm line.

In the analysis of zero-phonon lines, it is quite interesting that the temperature dependence of the intensity, peak shift and half-width of the zero-phonon lines are well described by using common effective Debye temperature. This implies that each effective Debye temperature obtained from zero-phonon analysis is one of the characteristics of the center, and difference between the effective Debye temperature for the 1044 and 361 nm lines probably suggests that the center responsible for the 980 nm band with the 1044 nm zero-phonon line is different from that for the 352 nm band with the 361 nm line. This is compatible with the conclusion in § 4, namely, the 352 nm band is due to the Cr-associated center while the 980 nm band to intrinsic color center  $\text{M}^-$ .

## § 6 Summary

Among the irradiation-induced absorption band in "pure" (undoped) MgO crystal, the 245, 288 and 572 nm bands have been already ascribed to  $\text{F}^+$ ,  $\text{Fe}^{3+}$  ion and F center, respectively. However, the origins of the 352 and 980 nm bands, both accompanied with the zero-phonon lines at 361 and 1044 nm, have been still argued by many workers. In the present work, the influence of the various impurities are

studied and the assignments are given for these bands, that is, the 352 nm band to a Cr-associated center and the 980 nm band to the intrinsic color center  $M^-$ .

Extra bands are observed at 370, 400, 460 and 1200 nm for Ni-doped crystal, details of which will be discussed in a separated article.

The magnitude of the effective Debye temperature obtained from temperature dependence of the absorption intensity, peak shift and the half-width of the zero-phonon lines agree to each other, i.e. 800°K for 1044 nm line and 652°K for 361 nm line, respectively.

Different effective Debye temperatures obtained for 1044 and 361 nm lines suggest that the 980 and 352 nm bands are caused by the different origins, which is compatible with the result of impurity study.

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