PHYSICAL REVIEW B VOLUME 37, NUMBER 5 15 FEBRUARY 1988-I

Optical transitions in neutron-irradiated $MgAl_2O_4$ spinel crystals

L. S. Cain,* G. J. Pogatshnik,† and Y. Chen
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6061

(Received 13 July 1987)

Neutron irradiation of $MgAl_2O_4$ spinel crystals produces an *F*-center absorption band in the uv accompanied by a broad absorption band in the visible region. Excitation and emission experiments identify the observed structure in the visible absorption band as optical transitions of transition-metal impurity ions perturbed by neighboring *F* centers. The perturbation of the *F* center increases the oscillator strengths for these transitions by more than 3 orders of magnitude. The results of these experiments suggest that the 480-nm emission band, previously attributed to the *F* center, is also due to a transition-metal impurity.

I. INTRODUCTION

Over the last ten years the study of color centers produced by various irradiation treatments in spinel ($MgAl_2O_4$) has led to an increased understanding of color centers in this material.[1–5] But the relatively complex nature of the structure has made the interpretation of the details of microscopic models for various optical transitions difficult. These complications include the presence of transition-metal impurities in all synthetically grown crystals. Iron concentrations are typically on the order of 100 ppm for some of the best crystals. In addition, Cu, V, Cr, Mn, and Co are present in concentrations of the order of 10 ppm. The spinel structure also shows cation disorder in that there is some mixing of Al ions on Mg sites and Mg ions on Al sites.[6] These complications make electron paramagnetic resonance data difficult to interpret so that EPR experiments have not been able to correlate any specific defect configurations with the observed optical transitions. Therefore, many of the absorption and emission bands in this material have been identified by analogy with the two parent species of the spinel structure, MgO and Al_2O_3. While in some cases the assignment by analogy works quite well, other aspects of the optical properties of defects in spinel are very different than those of the parent species.

The similarities between spinel and the parent species prompted our investigation of this material. Both MgO and Al_2O_3 form *F* and *F* aggregate centers after neutron irradiation. Many of these centers are efficient emitters over broad spectral regions, and may lend themselves to applications for tunable solid-state lasers. We had anticipated that similar treatment in $MgAl_2O_4$ would also lead to color centers with efficient luminescence, which, unfortunately, has not turned out to be the case. This aspect illustrates one of the more fundamental differences between the $MgAl_2O_4$ spinel and the parent hosts in that the luminescence of color centers is severely quenched in the spinel. Nevertheless, we have extended some of the previous work on neutron- and γ-irradiated crystals in order to examine factors such as neutron dose dependence on the formation of color centers, as well as the role of impurity ions in influencing the optical properties of the material. In Sec. II we review some of the basic properties of the spinel structure along with the types of defects which are present in the crystals. In Sec. III the optical absorption features of neutron-irradiated crystals will be examined. Of principal interest will be the *F*-center concentration as a function of neutron dose, and the interaction of *F* centers with impurities in the crystal. Changes in the optical-absorption spectra following various thermal annealing and optical bleaching treatments will also be presented. Results of emission and excitation spectra of color centers in $MgAl_2O_4$ will be shown in Sec. IV, and their implications will be discussed in terms of impurity ions perturbed by *F* centers.

II. $MgAl_2O_4$ CRYSTAL STRUCTURE

The $MgAl_2O_4$ spinel is a cubic insulating oxide used in a number of optical and electrical applications. The values of its physical parameters, such as its band gap, melting point, and index of refraction, are close to those of its constituent oxides. However, its relatively more complex structure leads one to expect a wider variety of possible point defects.

The $MgAl_2O_4$ structure has the cubic space group O_h^7 ($Fd3m$) with eight molecules per unit cell. The oxygens are nearly cubic close-packed. There are 32 octahedral and 64 tetrahedral interstices per unit cell. In a normal spinel, 8 tetrahedral interstices are occupied by Mg^{2+} cations and 16 octahedral interstices are occupied by Al^{3+} ions.[7] The small deviation of the oxygens from cubic close-packed distorts the lattice so that the tetrahedral interstices are enlarged and the octahedral interstices are narrowed and tilted. The Al-O and Mg-O distances are nearly equal, as compared to the ideal close-packed oxygen structure where the Al-O distance would be almost 14% greater than the Mg-O distance.[8]

The presence of two cations with differing charges leads to the possibility of numerous electron and hole traps. Three different kinds of vacant lattice sites in various charge states are possible types of defects. Site mixing (cation disorder) is known to occur in synthetic crystals with up to 25% of the Mg^{2+} sites occupied by Al^{3+} ions, with a corresponding number of Mg^{2+} ions on Al^{3+} sites.[6] This cation mixing produces centers of local positive and negative charge which can serve as electron or hole traps.

Stoichiometry is also important in $MgAl_2O_4$. The spinel structure can exist as a mixture[9] of MgO and Al_2O_3, $MgO{:}xAl_2O_3$, for values of x from 1 to 5. Excess Al^{3+} ions replace Mg^{2+} ions for $x>1$ and charge neutrality is expected to be maintained by the formation of cation vacancies. These vacancies have been shown to occupy octahedral sites.[10] X-ray fluorescence measurements on our crystals have shown that $x \simeq 1.02$, so that some of these nonstoichiometric defects may exist in our samples.

The spinel samples used in these experiments were obtained from the Union Carbide Corporation and were grown by the Czochralski method. X-ray analysis showed the samples to be good single crystals. Neutron activation analysis to determine impurity content was performed at the Oak Ridge National Laboratory. The predominant impurity was Fe (110 wt. ppm), with traces of Cr, Mn, Ca, K, P, Na, and V.

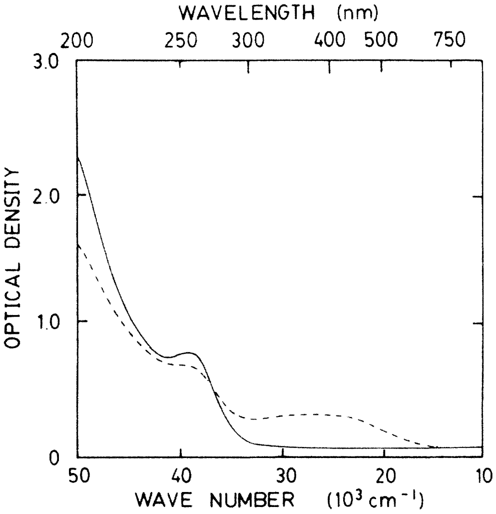

FIG. 1. The absorption spectrum of a 2-mm-thick $MgAl_2O_4$ spinel crystal. The solid curve shows the absorption of the Fe^{3+} charge-transfer bands in the as-received crystal. The dashed curve illustrates the growth of the visible absorption band and the reduction of the charge-transfer bands following a 15-min γ-ray irradiation using a ^{60}Co source.

III. ABSORPTION SPECTRA OF $MgAl_2O_4$

A. Crystal characterization

The absorption spectrum of spinel crystals prior to irradiation is dominated by the Fe^{3+} charge-transfer bands[1,2,11] at 39 500 and 52 000 cm^{-1} (8066 cm^{-1} = 1 eV). These allowed transitions occur at octahedrally coordinated Fe^{3+} sites in the spinel lattice as a result of the interaction of the *d* orbitals of the impurity ion with the neighboring O^{2-} ligands. Mössbauer studies have shown that there also exist Fe^{3+} ions at tetrahedral sites in the crystal,[12] which are approximately equal in number to those at octahedral sites for samples whose iron concentration was 0.1%. Similar studies in samples with somewhat higher Fe^{3+} concentrations (0.2–0.4%), showed the iron to occupy predominantly octahedral sites.[13] Iron impurities are also incorporated into the spinel lattice as divalent cations. These Fe^{2+} ions substitute for Mg^{2+} ions at tetrahedral sites in the crystal. The relative abundance of iron with differing charge states and symmetries seems to be strongly dependent on the concentration of the iron.[14,15] The existence of iron impurities in various charge states and site symmetries is expected to influence the optical absorption properties of these crystals following irradiation.

In order to characterize the effects of impurity ions in differing charge states on the absorption properties of the material we have subjected the crystals to ionizing radiation. The $MgAl_2O_4$ spinel single crystals were irradiated for 15 min at 320 K using a (1×10^6)-R/h ^{60}Co γ source at the Oak Ridge National Laboratory. Absorption measurements were performed at room temperature using a Perkin-Elmer Lambda-9 spectrophotometer. The absorption spectrum for the sample before and after irradiation is shown in Fig. 1. Before irradiation the absorption spectrum was dominated by the two Fe^{3+} charge-transfer bands as previously noted. Following γ-ray irradiation, the absorption of the Fe^{3+} charge-transfer bands was reduced and a new broad absorption band appeared at 25 000 cm^{-1} (400 nm). It has been proposed that the reduction of the Fe^{3+} charge-transfer bands is a result of electron capture by the iron impurities at these octahedral sites to form Fe^{2+} ions.[1]

Previous studies[1,3] have assigned the 25 000-cm^{-1} band to V-type centers (defects involving O^- ions due to the trapping of holes at O^{2-} sites) analogous to MgO. One of the more common hole trap centers in both MgO and Al_2O_3 is the V_{OH} center associated with OH^- impurities. This defect involves a Mg^{2+} or an Al^{3+} vacancy perturbed by an OH^- ion with one or two neighboring O^- ions. These centers typically have broad electronic transitions at energies near 2.5 eV (20 000 cm^{-1}). The transitions are attended by an ir absorption band near 3300 cm^{-1} associated with the vibrational stretching frequencies of the OH^- ions. Changes in the vibrational frequencies of these centers from trapping of holes following γ-ray irradiation are readily detected in MgO (Refs. 16 and 17) and Al_2O_3.[18] Therefore, changes in the visible optical absorption from the presence of V_{OH}-type centers following γ-ray irradiation should be accompanied by changes in the ir absorption spectrum as well.

To determine whether V_{OH}-type centers were partially responsible for the presence of the visible absorption band following γ-ray irradiation, we measured the infrared absorption spectrum of the spinel crystals before and after γ-ray irradiation. The measurements were made at room temperature using a Perkin-Elmer 983G ir spectrophotometer. The absorption spectrum prior to irradiation showed a strong absorption at 3335 cm^{-1} indicating the presence of OH^- ions in the crystal. After γ-ray irradiation, a difference spectrum showed no change in this region of the ir absorption. From these measurements we concluded that V_{OH}-type centers in spinel either do not exist or are not stable at room temperature, and therefore do not contribute to the visible absorption band. However, the lack of V_{OH}-type centers following γ-ray irradiation need not preclude the possibility that the 25 000 cm^{-1} band is due to other types of V centers. In fact, there is evidence that this band is correlated with a prominent isotropic electron paramagnetic resonance signal at $g=2.012$, presumably due to an unidentified hole center.[19]

B. Neutron-irradiated crystals

Single crystals of the $\mathrm{MgAl_2O_4}$ spinel were irradiated at the Oak Ridge National Laboratory National Low Temperature Neutron Irradiation Facility. The neutron flux varied between 3×10^{15} and 1×10^{18} neutrons $(n)/\mathrm{cm}^2$ for different samples. A typical absorption spectrum for the samples following neutron irradiation of 2×10^{16} n/cm^2 is shown in Fig. 2. In addition to the features which were present in the γ-irradiated crystals, there is also a prominent absorption band at 43 000 cm^{-1} attributed to F-type centers produced by the neutron irradiation.[4] If we assume that the low-energy shoulder on the F band is due to the presence of F^+ centers,[4] then the F center is the most prominent optically active defect associated with anion vacancies following neutron irradiation of $\mathrm{MgAl_2O_4}$.

The intensity of the F-center absorption band increased with exposure to the neutron flux, as shown in Fig. 3. The growth of the F-center concentration in $\mathrm{MgAl_2O_4}$ is similar to that observed in MgO (Refs. 20 and 21) and $\mathrm{Al_2O_3}$.[22] These anion vacancies in the oxides can capture one or two electrons to form F^+ and F centers, respectively. If we assume that the width of the absorption band is independent of the neutron dose, then the concentration of F centers is proportional to the peak absorption coefficient α_p. The absorption coefficient of F centers as shown in Fig. 3 exhibited a near-linear dependence with neutron flux. However, the growth became sublinear as the dose was raised above 1×10^{17} n/cm^2 due to saturation effects. In the $\mathrm{MgAl_2O_4}$ spinel we observed little evidence for the formation of optical bands attributable to cluster defects from neutron irradiation.

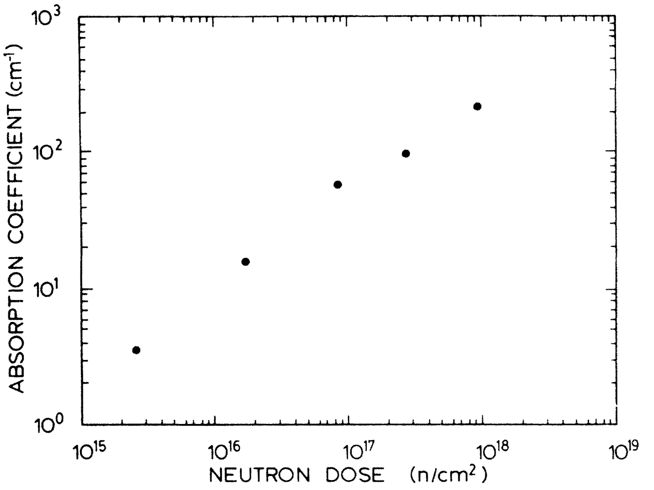

FIG. 3. The magnitude of the peak absorption coefficient of the F center as a function of neutron flux.

Neutron irradiation also altered the features of the absorption spectrum in the visible region. The changes in the absorption spectrum for various exposures to neutron flux are shown in Fig. 4. For the lowest neutron dose (3×10^{15} n/cm^2) the absorption spectrum looked very similar to the absorption spectrum of the γ-irradiated crystal. There was a reduction of the Fe^{3+} charge-transfer bands and the appearance of an absorp-

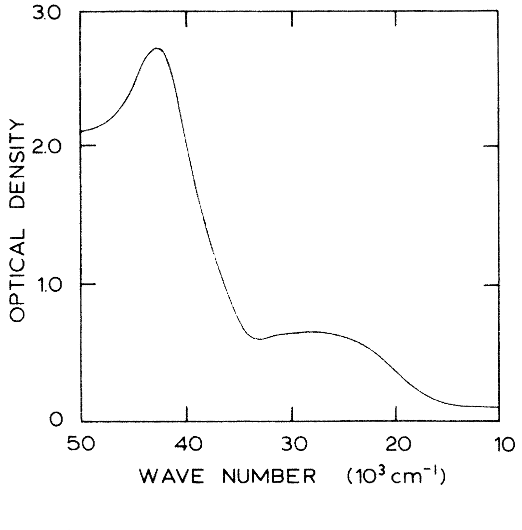

FIG. 2. The absorption spectrum of a 2-mm-thick $\mathrm{MgAl_2O_4}$ crystal after neutron irradiation at 2×10^{16} n/cm^2.

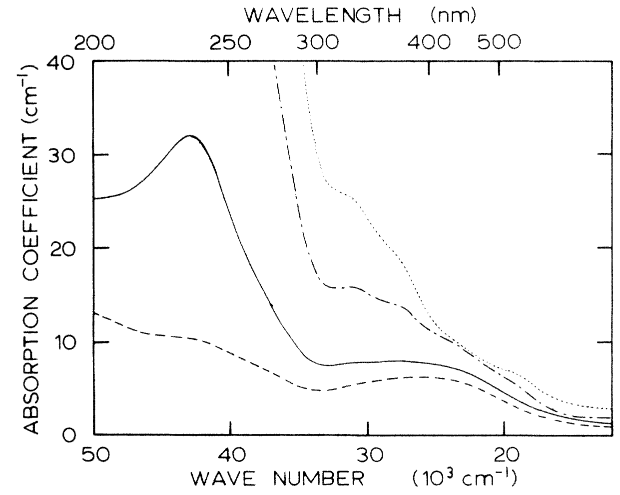

FIG. 4. The absorption spectra of the $\mathrm{MgAl_2O_4}$ spinel following neutron irradiation. The spectra are for samples irradiated at 3×10^{15}, 2×10^{16}, 1×10^{17}, and 3×10^{17} n/cm^2, in order of increasing optical density.

tion band at 25 000 cm^{-1}. There was only a small increase in the F-center absorption at 43 000 cm^{-1}. For a neutron flux of 2×10^{16} n/cm^2 the F band became the dominant feature of the absorption spectrum. The band in the visible increased slightly and it began to show a small amount of structure. As the neutron dose is further increased, these structural features became more apparent. The absorption bands that gave rise to the structure are the focus of excitation experiments described in Sec. IV. In addition, the underlying broad absorption band shifted to higher energy. This shift was somewhat difficult to characterize, however, and it could be due to the presence of an unresolved absorption band that begins to grow in at ~30 000 cm^{-1}.

C. Optical bleaching and thermal annealing

We shall present results on the optical bleaching of MgAl$_2$O$_4$ spinel crystals subjected to γ-ray or neutron irradiation, focusing on the bleaching of the 25 000-cm^{-1} band and the F band. Optical bleaching at visible wavelengths in both the γ- and neutron-irradiated crystals resulted in the reduction of the 25 000-cm^{-1} band. The subsequent change in the valence of the iron impurity to Fe^{3+} restored the charge-transfer bands to their original intensity. The efficiency of this photoionization process increased as the energy of the bleaching light increased from ~20 000 cm^{-1}. The efficiency reached a maximum near 31 000 cm^{-1} (~325 nm) and then decreased for shorter wavelengths. The appearance of a maximum in the bleaching efficiency at 31 000 cm^{-1} may be related to a peak in the photoconductivity near 330 nm observed in the irradiated spinel.[23] The photoconductivity signal could be due to the capture of holes from hole centers or perhaps even from the Fe^{2+} ions. However, at this time we cannot rule out the possibility that the visible absorption band may arise from transitions of the Fe^{2+} ions to the conduction band.

Optical bleaching into the F absorption band of the neutron-irradiated crystals also modified the absorption spectrum. This procedure resulted in the ionization of the F center, producing an F^+ absorption band as a slight shoulder on the low-energy side of the F band.[4]

The results of our thermal annealing experiments were similar to those obtained by White *et al.*[1] Thermal annealing from 100 to 300 °C resulted in the decrease of the absorption bands in the visible region of the spectrum. Various studies of thermoluminescence have shown that for temperatures between 200 and 300 °C, various glow peaks are identified with emission from transition metal impurities,[3,5] notably Cr^{3+} and V^{3+}. The emission results from the ionization of Cr^{2+} or V^{2+} ions which had served as traps for electrons released during irradiation. At temperatures between 300 and 500 °C, we observed that the absorption band of the F center began to anneal due to the recombination of the anion vacancies with the mobile oxygen atoms which had been displaced by the neutron bombardment. By 500 °C, almost all of the F centers had been annealed for the entire range of neutron exposures. There was also no sign of any type of F center clustering observed during the thermal annealing as there is in MgO and Al$_2$O$_3$. This is consistent with the observed lack of aggregate center formation for high neutron fluxes. It appears that cluster defects are not stable at room temperature, or are not optically active.

IV. EMISSION AND EXCITATION SPECTRA

A. Experimental procedure

Samples of the MgAl$_2$O$_4$ spinel which had been subjected to neutron irradiation exhibited several features in emission which differed from those observed in unirradiated crystals. In discussing these features, we will focus on three types of luminescent centers: the 720-nm emission band from Cr^{3+} transitions, the 520-nm V^{3+} emission, and the 480-nm emission band which has been previously attributed to F-center luminescence.

Both excitation and emission spectra for these transitions were measured at room temperature in a Spex Fluorolog 212 spectrofluorimeter. The emission spectra were obtained using a cooled Hamamatsu R928 photomultiplier tube. The excitation spectra were normalized to the incident light intensity by reference to the emission of a Rhodamine B dye solution. Both excitation and emission spectra were corrected for the response of the photomultiplier (PMT) and monochromators.

B. Cr^{3+} luminescence

The room-temperature emission spectrum of Cr^{3+} in the MgAl$_2$O$_4$ spinel consists of a series of sharp lines near 700 nm and a sideband which peaks near 720 nm.[24] The absorption spectrum of the Cr^{3+}-doped spinel shows an absorption band at 18 520 cm^{-1} (~540 nm) for the $^4A_2\rightarrow{}^4T_2$ transition, and a band near 25 600 cm^{-1} (~390 nm) for the $^4A_2\rightarrow{}^4T_1$ transition.[24,25]

The excitation spectra for Cr^{3+} in the spinel are shown in Fig. 5 for an as-received sample, as well as for

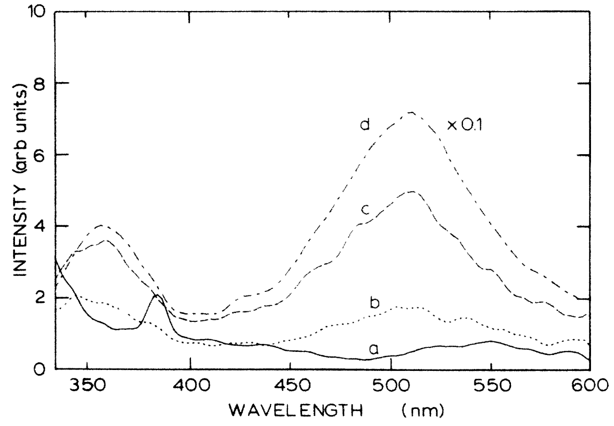

FIG. 5. Excitation spectra of the MgAl$_2$O$_4$ spinel for the Cr^{3+} emission at 720 nm for crystals with differing exposures to neutron irradiation. The excitation spectrum for the as-received sample (curve a), and crystals, irradiated with 2×10^{16} (curve b), 1×10^{17} (curve c), and 3×10^{17} n/cm^2 (curve d).

the neutron-irradiated samples. The spectra were obtained with the emission spectrometer tuned to 720 nm. The as-received sample [Fig. 5 (curve *a*)] showed two excitation peaks at 540 and 388 nm which correspond to the energies of the $^4A_2$ to $^4T_2$ and $^4A_2$ to $^4T_1$ transitions as described above. The intensities of the excitation peaks were very small, reflecting the low chromium concentration and the low oscillator strengths of the transitions. Figure 5 (curve *b*) shows the excitation spectrum for the chromium emission of the sample irradiated with a neutron flux of 2×10^{16} n/cm^2. The Cr^{3+} excitation spectrum had clearly been altered by the neutron irradiation. The 388-nm excitation peak began to be masked by new excitation bands. Again there were two excitation peaks, but they were shifted to higher energy compared with peaks in the as-received sample. In the sample irradiated with 1×10^{17} n/cm^2 [Fig. 5 (curve *c*)] the shift in the excitation bands was very clear. The new excitation peaks were at 360 and 515 nm. In addition to the shift to higher energies, the excitation peaks became much more intense. Figure 5 (curve *d*) shows the excitation spectrum of the 3×10^{17} n/cm^2 neutron-irradiated sample. The intensities of the optical transitions had increased by approximately 2 orders of magnitude above that of the as-received crystal.

It is unlikely that the reduction of the Cr^{3+} excitation bands in the as-received sample following neutron irradiation was caused by electron capture by the chromium impurity to form Cr^{2+}. This possibility can be dismissed on at least three grounds. First, the stability of Cr^{3+} makes it unlikely that all of the chromium ions end up as Cr^{2+}. Second, the excitation and emission spectra of Cr^{2+} should look different than that of Cr^{3+}. Our experiments showed the emission to be characteristic of Cr^{3+} and the excitation spectrum also looked like Cr^{3+} with a shift in energy. Finally, it is difficult to explain the dramatic increase in the strengths of the observed transitions as a function of neutron dose using a Cr^{2+} model.

A model which explains the observed features of the Cr^{3+} emission and excitation spectra is that of Cr^{3+} impurity ions perturbed by the presence of a nearby *F* center. Figure 6 shows a portion of the Tanabe-Sugano diagram[26] for Cr^{3+} The optical transitions from the $^4A_2$ ground state to the $^4T_2$ and $^4T_1$ excited states in the as-received spinel samples are depicted by the arrows at *a*. The presence of a nearby *F* center may modify the environment at the Cr^{3+} impurity site to produce an effective increase in the crystal field. The increased crystal field strength would shift the positions of the optical transitions to higher energy, as illustrated by the arrows at *b*. In addition to the shift in energy, the perturbation induced by the *F* center can increase the oscillator strength by introducing odd components to the crystal field, or by exchange coupling between the *F* center and the Cr^{3+} impurity. The enhancement of the oscillator strength by the exchange interaction has been previously observed between *F* centers and transition-metal impurity ions[27,28] in MgF_2 and RbMgF_3.[29,30]

The enhancement in the oscillator strengths of the Cr^{3+} transitions can be very large. We observed no saturation in the increased strength of the excitation peaks for the neutron-irradiated samples. In samples irradiated with 1×10^{18} n/cm^2, the enhancement in the oscillator strength of the Cr^{3+} transitions was greater than a factor of 1000. Therefore, only a fraction of a percent of the Cr^{3+} sites need to be perturbed in order to overwhelm the excitation peaks in the as received samples. As the concentration of *F* centers increased, the number of perturbed chromium sites also increased, so that the excitation peaks became more intense as a function of neutron dose. The strength of the perturbation on the Cr^{3+} transitions will depend on the relative positions between the *F* center and the impurity. Therefore we expect that the excitation bands will be inhomogeneously broadened due to the different possible positions that the *F* center can occupy with respect to the chromium ion.

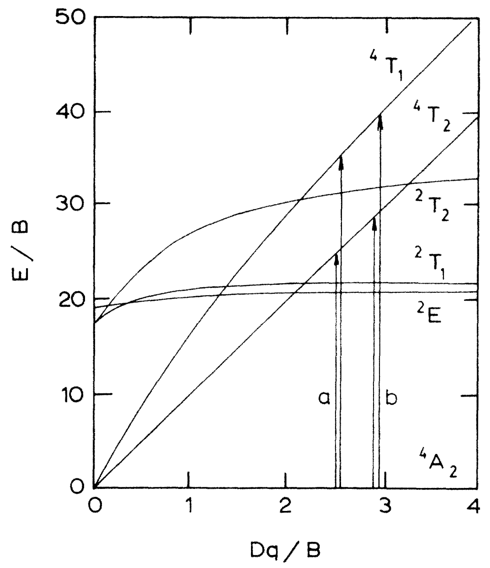

FIG. 6. Portion of a Tanabe-Sugano diagram for octahedrally coordinated Cr^{3+}. The arrows at *a* indicate schematically the positions of the $^4A_2\rightarrow{}^4T_2$ and $^4A_2\rightarrow{}^4T_1$ transitions in the as-received spinel crystals. The arrows at *b* reflect the change in these excitation energies due to the effective increase in the crystal field strength from the interactions with the perturbing *F* centers.

Unlike the case of the excitation peaks, very little shift in the emission energy for the perturbed chromium sites is expected. The emission, which results from the ^2E to $^4A_2$ transition, as shown in Fig. 6, should be almost independent of the strength of the crystal field. However, we observed small shifts introduced by the perturbations of the *F* centers which were sufficient to wash out much of the structure in the Cr^{3+} emission band, although there was not much of a shift in peak position.

The large increase in the oscillator strength of the Cr^{3+} transition is expected to produce a dramatic change in the fluorescence lifetime. As a further test of the model we measured the fluorescence lifetimes of the chromium emission in the as-received and neutron-

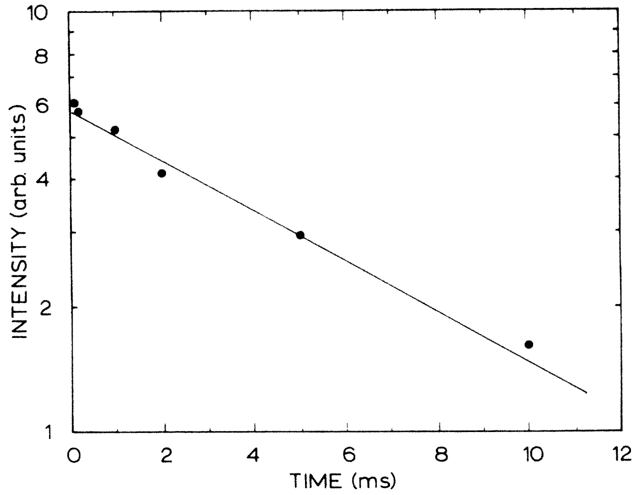

FIG. 7. The room-temperature fluorescence lifetime of Cr^{3+} in $MgAl_2O_4$. The experimentally determined lifetime is 8 ms.

irradiated crystals. The measurements were made using a phosphorimeter attachment (Spex Model 1934C) on the spectrofluorimeter, by varying the time delay between the gate pulse of a gated integrator and the output of a pulsed xenon lamp. The result of the lifetime measurement in the as-received crystal is shown in Fig. 7. Although the light signals were very weak, the lifetime at room temperature of 8 ms is quite reasonable. This is somewhat shorter than the lifetime measured by Wood *et al.* at liquid-nitrogen temperature.[24] However, these vibronically assisted transitions are expected to have shorter lifetimes at room temperature than at 77 K. The lifetime is also longer than that of ruby, where the trigonal distortion to the crystal field makes the transition more allowed than in the spinel. The results of the lifetime measurement in the sample irradiated with 1×10^{18} n/cm^2 are shown in Fig. 8. The fluorescence lifetime was reduced to about 14 μs, indicating a much more allowed transition. The large decrease in the fluorescence lifetime of the neutron-irradiated sample supports the model for the enhancement of the oscillator strengths of Cr^{3+} impurities perturbed by the presence of *F* centers.

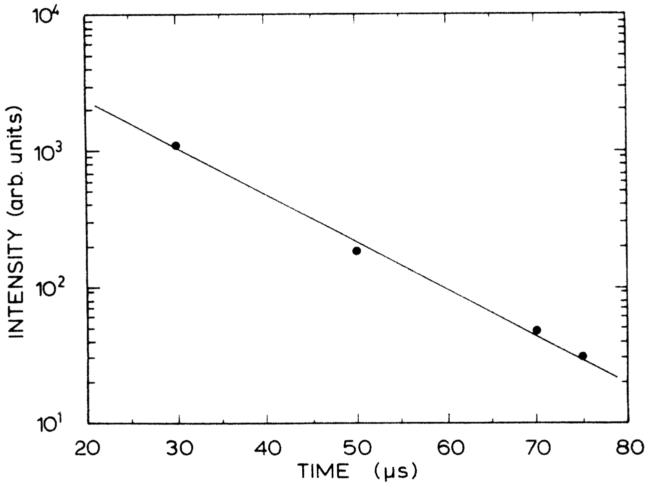

FIG. 8. The room-temperature fluorescence lifetime of Cr^{3+} in neutron-irradiated $MgAl_2O_4$. The neutron dose for the sample was 1×10^{18} n/cm^2. The experimentally determined lifetime is 14 μs.

C. V^{3+} emission

In addition to the chromium emission, we also observed emission from the presence of V^{3+} impurities. Fluorescence from V^{3+} in the spinel produces a broad emission band at 520 nm.[31] In the as-received samples, the vanadium emission was difficult to detect. However, in samples which were neutron-irradiated, the emission became easily detectable, and it exhibited a behavior similar to the chromium emission. The excitation band peaked at 400 nm and the intensity increased as a function of neutron dose. We therefore assume that the perturbation of the *F* centers on the V^{3+} impurities is analogous to the effect of the *F* centers on the Cr^{3+} impurities.

The enhancement in the oscillator strengths of transition-metal impurities also accounts for the observed structure on the broad visible absorption band following neutron irradiation. The chromium excitation bands lined up with small peaks in the absorption spectrum observed at 520 and 365 nm. The peak of the V^{3+} excitation band also corresponded to a small absorption peak. Therefore, the excitation measurements indicate that the structure on the visible absorption band following neutron irradiation, as shown in Fig. 4, was due, at least in part, to the strengthening of the optical transitions of impurities in the $MgAl_2O_4$ spinel. The peaks which were unaccounted for by the chromium and vanadium are probably due to other impurities whose luminescence is quenched.

D. The 480-nm emission band

Ultraviolet excitation of neutron-irradiated $MgAl_2O_4$ crystals resulted in an additional emission band at 480 nm. This 480-nm emission band had been tentatively identified as luminescence from the *F* center.[32] The assignment was based on excitation into the *F*-center absorption band with 240-nm uv light. The results of our study in neutron-irradiated crystals make this assignment questionable. While the excitation of our as-received and neutron-irradiated samples with 240-nm light produced at 480-nm emission band, excitation at this wavelength also produced Cr^{3+} and V^{3+} emission. The common excitation wavelength of these impurity ions does not rule out that the 480-nm emission is indeed that of the *F* center. However, we have found that the intensity of the 480-nm emission band following 240-nm excitation was nearly independent over 3 orders of magnitude of the *F*-center concentration. The emission was essentially the same in the as-received crystals. While Bandyopadhyay and Summers pointed out that some *F* centers could be present in the as-grown material,[32] this assignment cannot account for the near independence of the emission intensity over several orders of magnitude in *F*-center concentration.

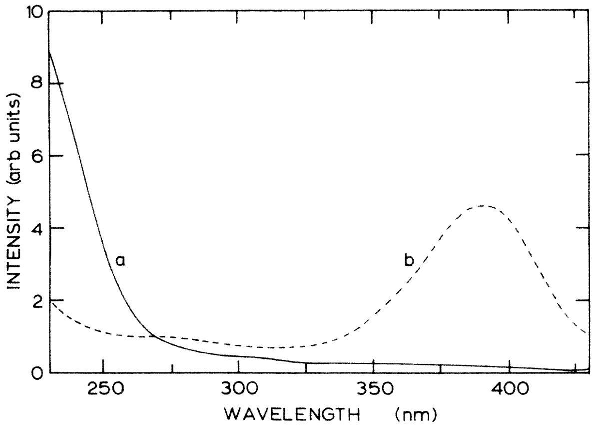

FIG. 9. The excitation spectrum of the 480-nm emission band in the $MgAl_2O_4$ spinel. Curve *a* is from an as-received crystal, and curve *b* is from a sample irradiated with 1×10^{18} n/cm^2.

Finally, the excitation spectrum of the 480-nm emission band for the neutron-irradiated crystals showed the same behavior as the excitation spectra of the Cr^{3+} and V^{3+} impurities. Figure 9 shows the excitation spectra of the 480-nm band in an as-received sample and a sample irradiated with 1×10^{18} n/cm^2. The emission was measured on the high-energy side of the 480-nm emission band, at 450 nm, to minimize complications resulting from the V^{3+} luminescence. The as-received sample had a single excitation band in the uv as shown in Fig. 9 (curve *a*). The neutron-irradiated sample also exhibited a weaker excitation band in the uv, but Fig. 9 (curve *b*) shows that there was an additional excitation peak at ~380 nm, far removed from the *F* band. This peak was not apparent in the as-received crystals, but as the exposure to neutron flux was increased, this 380-nm excitation band increased, analogous to the chromium and vanadium excitation bands. These excitation measurements were complicated by the luminescence of other centers in the neutron-irradiated crystals. To verify that the excitation spectra shown in Fig. 9 were due to the same center, we measured the emission spectrum in the two crystals under the same conditions as the excitation measurements. Figure 10 (curve *a*) shows the 480-nm emission band in the as-received crystal from 240-nm excitation. Figure 10 (curve *b*) shows the emission spectrum of the neutron-irradiated crystal with 375-nm excitation. The bands have been normalized to the same peak intensity for comparison. The similarity of the two emission bands under these extremely different conditions gave us confidence in the validity of our results from the excitation experiments. The results of these emission and excitation measurements indicate that the 480-nm emission band resulted from the luminescence of an unidentified impurity ion coupled to an *F* center, and not from intrinsic *F*-center fluorescence.

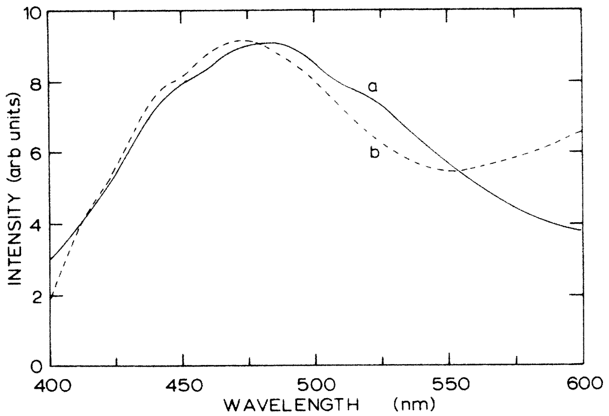

FIG. 10. The emission spectrum of the 480-nm emission band in spinel. Curve *a* is from an as-received sample excited at 240 nm, and *b* is from a sample irradiated with 1×10^{18} n/cm^2 with 375-nm excitation.

V. SUMMARY

The results of our investigations in the $MgAl_2O_4$ spinel emphasize the importance of trace amounts of impurities in nominally pure optical crystals. Gamma-ray irradiation of the spinel resulted in changes in the optical absorption spectrum of the crystals associated with the valence change of iron impurities. This procedure produces absorption in the visible, near 25 000 cm^{-1}, and a concomitant decrease in the Fe^{3+} charge-transfer bands.

Neutron irradiation of the spinel crystals produced a broad absorption band in the uv due to the creation of *F* centers. These *F* centers interact with impurity ions to alter the absorption properties in the visible region. Exchange coupling between the *F* centers and impurities greatly increased the oscillator strengths of the optical transitions within the *d* manifold of the impurity ions, making these transitions more allowed. These effects were clearly demonstrated by the increased intensities of the impurity excitation bands associated with the growth in the *F*-center concentration. The substantial reduction in the Cr^{3+} fluorescence lifetime in the neutron-irradiated crystals supports this contention. These interactions account for the observed structure in the visible absorption spectrum of the neutron-irradiated crystals.

Finally, the results of various excitation and emission experiments lead us to conclude that the 480-nm emission band in the $MgAl_2O_4$ spinel was not that of the *F* center. This emission band was probably due to a transition-metal impurity perturbed by an *F* center, analogous to the observed behavior of Cr and V in these irradiated crystals.

ACKNOWLEDGMENTS

The authors would like to thank Victor M. Orera for helpful discussions. One of us (L.S.C.) was supported in part by an appointment to the U.S. Department of Energy Faculty Research Participation program administered by Oak Ridge Associated Universites. This research was sponsored by the U.S. Defense Advanced Research Projects Agency under Interagency Agreement 40-1611-85 with Martin Marietta Energy Systems, Inc., Contract No. DE-AC05-84OR21400 with the U.S. Department of Energy.

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*Permanent address: Department of Physics, Davidson College, Davidson, NC 28036.

†Also at North Carolina State University, Raleigh, NC 27695.

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