

only by the change of the occupation in vibrational levels. With increase in temperature, the higher vibrational levels in the excited state are made occupied due to thermal excitation. This causes the emission peak to move to higher energy, if the excited state vibration is different from the ground state vibration. In the case of the excitation spectrum, the occupation in the higher vibrational levels make the excitation peak move to lower energy contrary to the case of the emission spectrum.

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Studies of Point Defects in Magnesium Oxide*

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This study is an attempt to correlate optical absorption bands in single magnesium oxide crystals with point defects known to exist from electron spin resonance observations. Optical measurements in the range of 4000 to 50000 cm^{-1} were made on crystals as received, after heat treatments, after ultraviolet or X-irradiation, and after neutron irradiation, with subsequent heat treatment or irradiation. Our goal has been the assignment of optical bands as due to impurities in particular valence states, to trapped hole centers or trapped electron centers. Some progress has been made by comparison of optical and ESR spectra on the same crystals. The point defect for which the correlation of behavior of the two types of spectra is best is the single hole trapped on an oxygen ion adjacent to a positive ion vacancy. The absorption band which we ascribe to this center occurs at 18500 cm^{-1} , and is responsible for the fleeting violet color of MgO crystals upon irradiation. While neutron irradiation gives rise to *F*-centers (electrons trapped at negative ion vacancies) and to visible coloration, no assignment of optical bands with particular electron trapping centers has yet been made.

Introduction

The results of previous optical studies of magnesium oxide can be classified mostly as effects of an oxide host on the properties of impurity ions of transition metals. For most such ions, the absorption coefficients are relatively small. However, a few impurity bands are so intense as to constitute a nuisance in the study of other bands. The most prominent are a pair at 34700 and 46000 cm^{-1} due to Fe^{3+} ^{1, 2)}. Since iron is omnipresent in available MgO samples, one must eliminate these bands by such treatment as heating in vacuum or in hydrogen at temperatures of 1200°C or higher to convert the iron to the Fe^{2+} state. However, irradiation with

39400 cm^{-1} light or with X-rays again will give large concentrations of Fe^{3+} . Also commonly present is Cr^{3+} , which shows a band at 5.9 eV, strongly overlapping the 5.7 eV band of Fe^{3+} ¹⁾. Strong bands at 6.3 and 6.9 eV have also been attributed to impurities³⁾. The absorption intensity of this group of bands is such that a number of authors have been deceived into assigning the absorption to MgO itself.

Of the impurity ions observed in MgO, those of vanadium, chromium, iron, cobalt and nickel readily are converted to alternative valence states. Chromium and vanadium exist preferentially in the trivalent state, though the divalent form of each results temporarily on X- or UV-irradiation. The significance of the presence of impurities which tend to be in the trivalent state when crystals are formed from the melt is that positive ion

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vacancies are also incorporated in appreciable numbers. The number of vacancies can be considerably increased by heating in oxygen. These vacancies profoundly affect the behavior of the crystal on UV- or X-irradiation, since they serve as traps for positive holes, as is shown later. Another very significant group of defects in MgO formed on irradiation are the monovalent ions of iron, cobalt and nickel, with Fe^{1+} being most important because of the universal presence of iron.⁴⁾ This emphasis upon impurity effects in MgO is in sharp contrast with that in the alkali halides, where impurity studies have played a subsidiary role. For MgO, no optical absorption spectra of F -centers or of V -centers have previously been correctly identified⁵⁾⁻¹²⁾. Optical or X-irradiation, electrical treatment or heating in metal vapors do not produce negative ion vacancies in detectable numbers, and hence no F -centers are seen. The only very effective technique for crystals is neutron irradiation, which produces the requisite atomic displacements¹³. More complex types of F -centers are also produced by neutron irradiation¹⁴⁾.

MgO is colored by UV- or X-irradiation, but we cite evidence here that this coloration is correlated with trapped hole centers. The simplest such center has a hole localized on an oxygen ion adjacent to a positive ion vacancy, as is shown by ESR data. (V_1 center)¹⁵⁾. The antimorph of the F' -center is one with two holes trapped at a positive ion vacancy¹⁵⁾. By analogy we shall call it a V' center. It is too unstable to exist at room temperature, presumably, decomposing into V_1 centers. Other more complex V -centers are produced by neutron irradiation¹⁴⁾.

Experimental

Our undoped samples embraced a wide range of impurity concentrations, the purest having 3ppm iron as the major transition element impurity. Absorption measurements were made on a Cary Model 14R spectrophotometer, using neutral density screens to extend the range to absorbances approaching 6, though usually between 5 and 6 one has serious troubles with scattered light or from luminescence phenomena. A hole cut in the front of the Cary sample compartment made it possible to carry on irradiation at arbitrary

wavelengths without moving the crystal out of the spectrophotometer. This was achieved by turning the crystal through some angle with respect to the axis of the spectrophotometer. A grating monochromator was generally used for selection of the irradiation wavelength region.

Neutron irradiation doses of fast neutrons were in the range of 3.8×10^{18} nvt to 1.5×10^{20} nvt. Irradiation occurred at pile temperatures.

When MgO crystals were heated either in vacuum or in hydrogen an HCl-insoluble brownish substance deposited on the silica walls of the furnace. This material has been submitted for spectral analysis. Heating at 1500°C in hydrogen for an hour was sufficient to reduce absorbance of a 3mm crystal to 0.2 or less at 5eV.

Electron spin resonance measurements were made at 9.2 Gc/sec, either at 20°K or at 77°K to monitor the concentrations of various centers presumed to give rise to the absorption being measured.

Numerous X-irradiation experiments were carried out either with 30 or with 50 kV sources. Samples were nearly always wrapped in aluminium foil, since some centers are bleached by visible light.

Results

1. Non-Irradiated Samples

The absorption bands occurring most frequently in untreated MgO crystals are listed in Table I. Heating in vacuum above 1200°C (or better, in hydrogen) bleaches MgO to the extent that one does not reach an absorptivity of 1/cm until about 45000 to 47000 cm^{-1} . Residual bands after H_2 treatment are also indicated in Table I. The band listed at 41000 cm^{-1} is not resolved, appearing as a shoulder.

Although many measurements have been carried out at energies above 5 eV, the results are not given here. In our spectrophotometer one has considerable difficulty from luminescence at high energies.

2. Ultraviolet and X-Irradiated Samples

Many MgO crystals when subjected to 39420 cm^{-1} or X-irradiation show a violet color associated with an 18500 cm^{-1} absorption band. In many untreated crystals one sees a brownish color on UV- or X-irradiation. This is seemingly due to combined absorption at

Table I.

Band Center	Typical Absorptivity	Half-width (cm ⁻¹)
Crystal as received		
1.2 eV 9700 cm ⁻¹	0.01/cm	1600
1.45 11700	0.005	1600
2.7 21800	0.01	4400
3.1 25000	0.01	3100
4.3 34700	0.1–20	3100
After H ₂ treatment		
1.2 eV 9700	0.01	1600
1.45 11700	0.005	1600
S* 5.1 41000	0.40	2500
After x- or 4.9 eV irradiation		
0.93 eV 7500	0.30	~100 (78°K only)
1.15 9300	0.02	~100 (78°K only)
2.3 18500	2.0	8800
4.3 34700	1–20	3100
3.2 25800**	2	8100
3.7 29800**	2	5600

* S implies a shoulder instead of a resolved peak.

** Inferred from line shape analysis.

18500, 25800 and 29800 cm⁻¹.

Heating in vacuum or in hydrogen at 1200°C or more diminishes the 25800 and 29800 cm⁻¹ absorption and eventually causes all MgO crystals we have treated to become violet after irradiation. However, the 25800 and 29800 cm⁻¹ bands are not completely lost. The 18500 cm⁻¹ band is greatly increased in intensity on heating the crystal in oxygen at 1200°C or more.

To test our hypothesis that the optical band at 18500 cm⁻¹ arises from the same center which we observe in electron spin resonance and attribute to the V₁ (trapped hole adjacent to a positive ion vacancy), we made ESR and optical measurements in rapid succession on the same crystal after appropriate treatments. First a relatively pure crystal (iron less than 10 ppm, labeled as PI) was X-irradiated. After both types of spectrum were run, it was heated at 100°C for a short time and both measurements were repeated. Two subsequent heating periods at 100°C were employed. The measured intensities relative to the original were as follows:

	Intensity of 18500 cm ⁻¹ peak	ESR Intensity of V ₁ Center
Initial measurement	100	100
After first 100° heating	88	123
After second 100° heating	42	31
After third 100° heating	7	7

Optical intensities were measured by isolating a gaussian curve centered at 18500 cm⁻¹. ESR intensities were measured relative to a Mn²⁺ spectrum in the same sample; this spectrum does not appear to be altered in intensity by these treatments.

3. Neutron-Irradiated Samples

After neutron irradiation, magnesium oxide crystals show a strong absorption band at 17600 cm⁻¹. In the interval 34500 cm⁻¹ to 37000 cm⁻¹ the absorptivity rises from about 50/cm to over 200/cm. A spectrum is given in Fig. 1, and a tabulation of peak locations for one crystal is given in Table II. Intensities are not to be read from Fig. 1 or 2, since the strongest peaks have been suppressed to show structural details. With one exception, the spectra of most neutron irradiated crystals is essentially similar. The exception is a crystal of unusually low iron content, (PI), as judged by electron spin resonance measurements of Fe³⁺. This crystal shows some lines which appear in others only after heating.

Fig. 2 shows the spectrum of a similar crystal which was heated for 500 hours (in air) at 400°C. This temperature was chosen on the basis of ESR results which indicated that one could still recover most of the original F-centers by X-irradiation.

We have sought to establish correlations between neutron-induced bands by selective bleaching. Irradiation was begun in the 9570 cm⁻¹ band, followed in succession by irradiation in each of the major bands, progressing toward higher energies. Very little change in the spectrum could be established by irradiating in any of the resolved bands. Upon irradiating with the 39420 cm⁻¹ mercury line, there was a small increase in intensity of the bands at 23600, 19000 as well as those in the region of 10000 cm⁻¹.

Table II. Bands induced by neutron irradiation

<i>As Irradiated</i>			<i>After 400°C Heating</i>		
<i>Band Center</i>	<i>Absorptivity</i>	<i>Comments</i>	<i>Band Center</i>	<i>Absorptivity</i>	<i>Comments</i>
33000 cm ⁻¹	0.7/cm		S 33000 cm ⁻¹	0.7/cm	
28300	20		28300	4.0	Decreased
S* 28100	0.2		S 28100	0.2	Decreased
S 27900	0.4		S 27900	0.2	Decreased
S 27850	0.8		S 27850	0.4	Decreased
27600	1.5		27600	1.0	
26300	0.6		26300	0.8	Broad
26000	0.6	Fairly Sharp			
25400	0.2	Fairly Sharp			
24200	0.6		24200	0.3	Greatly Decreased
23600	3.0		23600	0.1	Greatly Decreased
22200	0.2		22200	3.0	Greatly Increased
			S 22000	0.1	
21800	0.1		21800	0.4	Greatly Increased
			21700	0.4	
			21600	0.2	
21400	0.2		21400	2.0	Very Greatly Inc.
			21300	2.5	
19100	0.6		20500	0.2	
			19100	1.2	
17600	40	Most Intense; Broad	S 17800	0.2	
			17600	5.0	New Sharp Peak
			S 17100	0.2	
			16800	40	Most Intense Peak
			S 16500	0.5	
			S 16300	0.5	
			S 16050	0.2	
			16000	2	
			15900	1.5	
15600	0.2		15600	15	Greatly Increased
15400	0.1		15400	3	Greatly Increased
			S 15200	0.1	
			14900	0.3	
			14600	0.2	
14200	0.1		14200	2	Greatly Increased
S 12400	0.1				
S 12000	0.2				
11000	0.1		11000	0.1	
10700	0.2				
10300	1.0		10300	0.5	
			10100	0.1	
9950	2.0		9950	0.7	
			S 9850	0.2	
			S 9750	0.1	
9570	6		9570	4	
8600	0.2		8600	0.1	

* S indicates a shoulder instead of a fully resolved peak.
Values of absorptivity less than 0.5 are approximate.

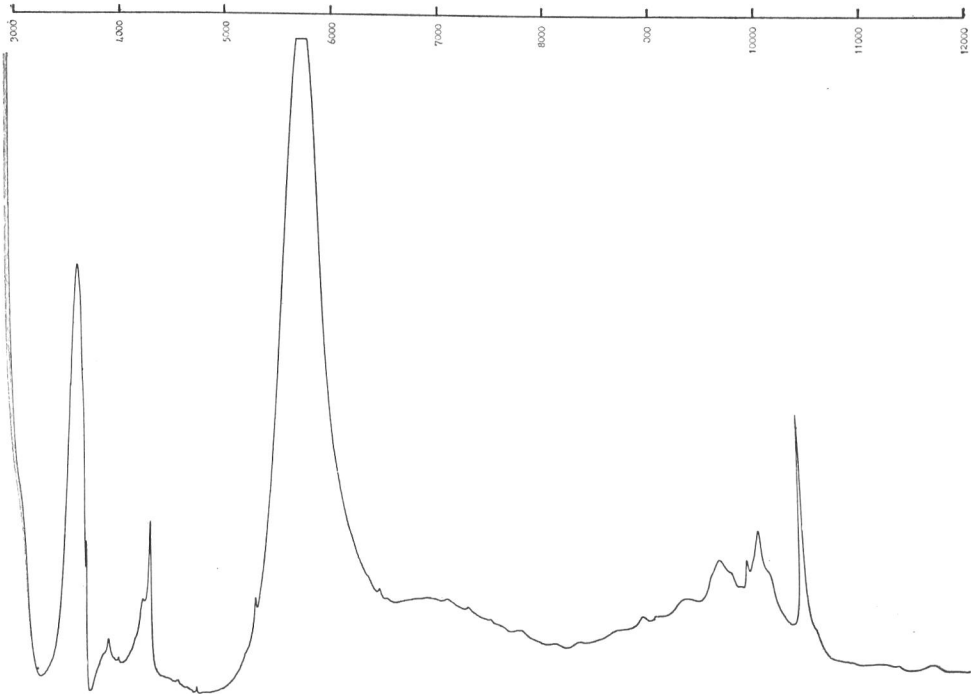


Fig. 1. Absorption of neutron-irradiated MgO at 78°K. Dose approximately 3×10^{19} nvt. The intensities are not accurately given here, since the heights of the strong peaks have been artificially reduced to keep all lines on scale. Wavelength scale is given in Å.

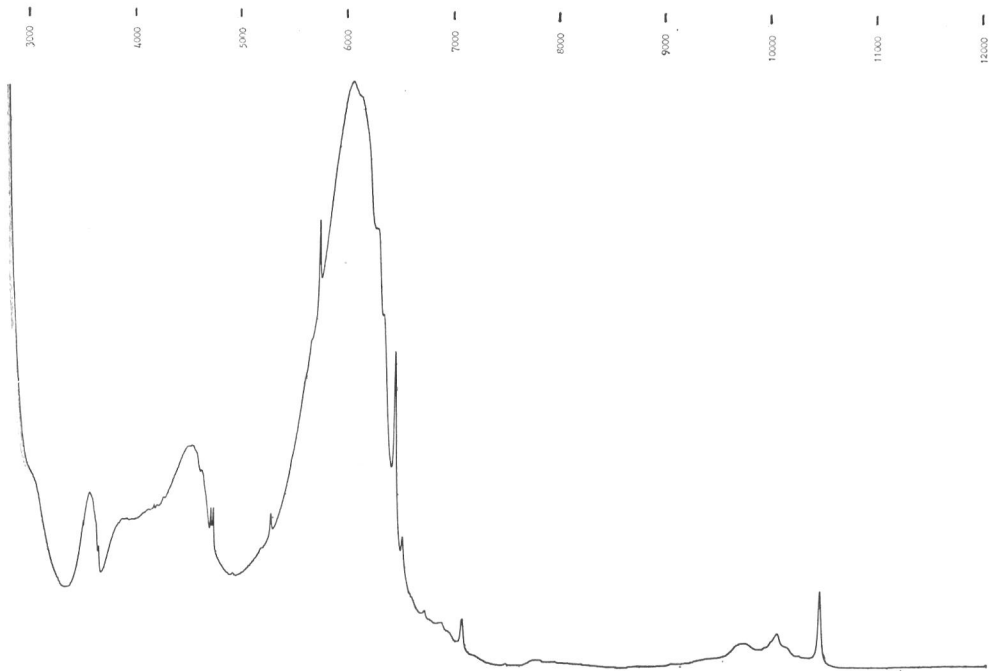


Fig. 2. Absorption spectrum of neutron-irradiated MgO after heating 500 hours in air at 400°C. Intensities of the strong peaks are far greater than shown here (see legend for Fig. 1).

Discussion

1. Impurities

Low and Weger¹⁶⁾ had originally suggested that a weak band near 10000 cm^{-1} was due to Fe^{2+} , observing that it was enhanced in intensity by heating in H_2 . We find two bands in this region rather than one, centered at 9700 and 11700 cm^{-1} , with intensities changing in parallel fashion.

Since our crystals were undoped, the absorption by impurities other than Fe^{3+} was very small at energies less than 40000 cm^{-1} , and no other impurity assignments were made in unirradiated crystals.

2. Ultraviolet or X -Irradiated Samples

Perhaps the most significant result of this paper is the linking of the 18500 cm^{-1} band-responsible for the visible color of MgO upon irradiation with the V_1 trapped hole center identified by ESR studies. In the optical data there is a question about the intensity of an overlapping band of uncertain half-width centered at about 29800 cm^{-1} . In the ESR case there are problems with orientation (the V_1 spectrum is anisotropic) and of overlapping with other ESR lines. We feel confident there was some source of uncontrolled difficulty with the second ESR measurement.

Although the data are far from precise, it does appear that the number of V_1 centers (positive holes trapped on oxygen ions adjacent to a positive ion vacancy) as determined from electron spin resonance and the intensity of the 18500 cm^{-1} band parallel one another. We thus suggest that the 18500 cm^{-1} band represents the optical absorption of V_1 centers.

The intensity of the 18500 cm^{-1} band and also of the ESR spectrum of V_1 centers increases after heating in oxygen at 1200°C , with subsequent irradiation. This will be expected, since thereby the number of positive ion vacancies in the crystal is increased, affording more hole sites for trapping.

3. Effects of Neutron Irradiation

Judged by ESR spectra, the most prominent point defect produced by neutron irradiation is the electron trapped at a negative ion vacancy. Hence the primary focus of optical absorption measurements is establishment of the location of the F -band. Secondarily, one would like to locate an F' band, corresponding

to the trapping of two electrons at one vacancy. We had hoped that by heating at 400°C one would empty shallow electron and hole traps, thus simplifying the optical spectrum. As shown in Table II and Fig. 2, the number of prominent resolved bands and shoulders is considerably increased.

Perhaps the most prominent change occurring in the optical spectrum upon heating the neutron-irradiated MgO to 400°C is the reduction in intensity of the visible band at 17600 cm^{-1} and the growth of a band of similar shape at 16800 cm^{-1} . This is doubtless associated with the transformation of one center into another.

As far as the crystal itself is concerned, we are aware of only one process occurring as low as 400°C (excluding bleaching of unstable centers). This is a diffusion of positive ion vacancies, as inferred from effects on ESR spectra. We have observed that heating at 400°C of MgO crystals containing F -centers gives rise to F_2 centers, an electron trapped at a vacancy pair¹⁴⁾. Presumably, the formation of F_2 - from F -centers can take place at an appreciable rate at temperatures such that positive ion vacancies have sufficient mobility.

Subsequent to the 400°C heating of neutron-irradiated crystals, UV-irradiation slightly increases absorption from 19000 cm^{-1} to higher energies without gain or loss of any bands. The peak at 16800 cm^{-1} remains in the same position, indicating that the changes on 400°C heating are irreversible by UV-irradiation.

Heating neutron-irradiated MgO crystals causes qualitatively similar reductions in intensity of the F -center absorption and of the 17600 cm^{-1} absorption band. Likewise, there is qualitatively parallel behavior in growth of F_2 -centers in ESR spectra and of the 16800 cm^{-1} band upon heating. More quantitative experiments are in progress to clarify the relation of the two optical bands to one another and to electron-trapping centers found by electron spin resonance.

It is possible that numerous displaced atoms may serve as electron or hole traps. However, unless the electric field symmetry is rather high, and is identical for a sufficiently large number of atoms, the ESR spectrum from such atoms may be lost in a maze of

lines from other centers.

One may speculate that a considerable number of optical bands may arise from displaced impurity atoms in various valence states. It is more than possible that some less common valence states of transition metal ions may be involved. We have already referred to the ionic states Fe^{1+} , Co^{1+} , Ni^{1+} found in $\text{MgO}^{(4)}$. Other unusual ions may also be present. In sites of purely cubic symmetry characterizing most substitutional ions in MgO , many possible transitions are symmetry-forbidden. After atomic displacement by neutron bombardment, many impurity atoms will doubtless be in sites of lower symmetry, and symmetry restrictions will be lifted. We are pursuing this hypothesis to see if apparent correspondences can be verified.

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DISCUSSION

Lidiard, A. B.: You assign the band at 2.3 eV to the hole trapped at an oxygen ion neighbouring a vacancy and this you say is an axial center. Is there any sign suggesting that illumination in this band can lead to reorientation of the centers, as *e. g.* by inducing dichroism by polarized illumination?

Wertz, J. E.: Experiments in this direction are now under way.

Matumura, O.: I would like to know the reason why two-hole center shows a paramagnetic resonance. Usually two-hole or two-electron center is non-magnetic.

Wertz, J. E.: A distinction must be made between two electrons in a single negative ion vacancy and two holes located on *separate* oxygen ions about 4.2 Å apart on opposite sides of a positive ion vacancy (V_1' center). Electron spin resonance spectra show these holes have a dipolar coupling. Hund's rule applied to two positive holes in this defect gives the unpaired state as the one of lower energy.

Uchida, Y.: According to our experiment the luminescence spectra of MgO under discharge excitation show two ultra-violet bands at 5.8 eV and 5.3 eV, which appear only at low temperature and are much enhanced in samples fired in oxygen. Whether there exists any relation between these bands and your 2.3 eV absorption seems to me interesting. I would like to know if you have studied the cathodoluminescence of MgO .

Wertz, J. E.: We assign the absorption band at 2.3 eV to the V_1 center. We do not as yet know the origin of the cathodoluminescence bands referred to.