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Charge-Transfer Spectra of Fe^{3+} and Mn^{2+} in Synthetic Forsterite (Mg_2SiO_4)[1]

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Abstract

The optical absorption spectra of nominally pure and Mn-doped Czochralski-grown single crystals of Mg_2SiO_4 have been measured from 1 eV to ~ 7.5 eV. The intensity of weak optical absorption bands at 4.78, 6.0, and 6.6 eV in the nominally pure crystal has the same dependence upon irradiation with gamma rays and subsequent thermal treatments as does the intensity of the electron paramagnetic resonance (EPR) spectrum of Fe^{3+} located in the forsterite $M(2)$ site. On the basis of this correlation, it is assumed that the optical bands are due to the Fe^{3+} ion. Oscillator strengths, calculated on the basis of the concentration of Fe^{3+} ions, are 0.2, 1.0, and 0.5 for the 4.78, 6.0, and 6.6 eV bands, respectively. These strengths are those expected for charge-transfer bands. The optical absorption spectrum of the Mn-doped crystal has an intense band at 6.5 eV and an indication of another at >7.3 eV. If it is assumed that the 6.5 eV band is due to a transition involving Mn^{2+}, then its oscillator strength is 0.1, and hence this band is attributed to a charge-transfer transition involving Mn^{2+}. Tentative estimates of Dq are $Dq(Fe^{3+}) \approx 1050\ cm^{-1}$ and $Dq(Mn^{2+}) \approx 850\ cm^{-1}$.

Introduction

Crystal-field spectra of divalent manganese, Mn^{2+}, have been observed in some natural minerals of the fayalite-tephroite sequence (Burns, 1970). To our knowledge, absorption bands due to charge-transfer processes have not been identified in these minerals nor in natural forsterites which contain ~0.1 wt % Mn^{2+} (Burns, 1970). Optical absorption bands with energies between 2.9 and 3.1 eV and an absorption band at 4.6 eV, observed in synthetic crystals, have been attributed to crystal-field and charge-transfer transitions, respectively (Shankland, 1969). In many crystals, absorption at energies ≥3 eV is too intense for measurements to be made (Burns, 1970; White and Keester, 1966) and is usually attributed to charge-transfer processes. Confirmation of the identification of 4.6 eV band, identification of additional charge-transfer bands due to Fe^{3+}, and identification of charge-transfer bands due to Mn^{2+} will be useful for future experimental and theoretical analyses of both crystal-field and charge-transfer spectra of d^5 ions in silicate compounds.

Charge-transfer spectra of Fe^{3+} in a number of oxide compounds in which the ion is in an octahedral crystal field have been measured (Tippens, 1970; Lehmann and Harder, 1970; Wickersheim and Lefever, 1967); and in some oxides in which the ion may occupy a tetrahedral crystal site, observed spectra have been attributed to Fe^{3+} in such sites (Lehmann, 1970; McClure, 1959). Data on the charge-transfer spectra of Mn^{2+} in octahedral environments in oxide compounds are less abundant. It is evident (Ballhausen, 1962) that these bands will have energies >4 eV for the high-spin cases.

Since the crystals on which the measurements described below were made contain higher concentrations of Fe^{2+} than of Fe^{3+}, the charge-transfer bands of Fe^{2+} may contribute to the observed spectra. Charge-transfer transitions of Fe^{2+} will have higher energies than those of Fe^{3+} (Ballhausen, 1962), and hence they may have energies exceeding the maximum energy to which measurements have been made. With respect to the spectra of Fe^{3+} in silicate crystals, there is also the problem of distinguishing

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between bands due to Fe^{3+} in octahedral and in tetrahedral crystal fields. As will be discussed below, there is a reasonable basis for assigning Fe^{3+} ions in crystals upon which the measurements reported here were made to one of the octahedral sites. In SiO_2 (α-quartz), energies of the first two charge-transfer bands are 5.1 and 6.23 eV when Fe^{3+} is in an interstitial site with a tetrahedral crystal field (Lehmann, 1971), and in the octahedral field of MgO these energies are 4.3 and 6.2 eV (Soshea, Dekker, and Sturtz, 1958).

The electron paramagnetic resonance (EPR) spectrum of Mn^{2+} has been observed in natural and synthetic Mg_2SiO_4 single crystals (Chatelain and Weeks, 1970, 1973; Gaite and Michoulier, 1970), and on the basis of the EPR parameters >95 percent of the ions occupy the $M(2)$ site (Birle *et al*, 1968). EPR spectra attributable to Fe^{3+} have not been observed in natural crystals, but were detected and analyzed in the case of synthetic crystals used in this work (Chatelain and Weeks, 1973). Chatelain and Weeks (1973) found that the EPR parameters and the effect of irradiation with energetic photons (^{137}Cs gamma rays) were consistent with an assignment of Fe^{3+} to the $M(2)$ site.[2] Trivalent iron in other sites was not detected. On the basis of the sensitivity of the EPR spectrometer, the fraction of Fe^{3+} ions in other sites was <0.05. Thus the Fe^{3+} and Mn^{2+} ions occupy only one crystal site in the synthetic crystals on which the measurements reported here were made.

Experimental

Samples

Crystals of nominally pure Mg_2SiO_4 and doped with 0.1 wt percent MnO were grown, using the Czochralski method, by pulling from the melt in air (Finch and Clark, 1971). The crystals, ~0.8 cm in diameter and >1 cm in length, were colorless and, except for a translucent core ~0.1 cm in diameter, were free of visible inhomogeneities at a magnification of 80×. The starting materials were powdered MgO (Kanto Chemical Company, nominal 99.99% MgO) and SiO_2 (Gallard Schlesinger Company, nominal 99.999% SiO_2). Impurities in samples cut from the boules were determined by arc spectroscopy (J. R. Sites, Analytical Chemistry Division, ORNL) and are given in Table 1.

For the case of the nominally pure crystal, the concentration was also measured by comparing the intensities of the EPR spectral components of Mn^{2+} with those in a standard. The value for the concentration obtained by this method is 1 ppm by weight of Mn, which agrees within error with the value in Table 1. Using the EPR components of Mn^{2+} as an internal standard, the concentration of Fe^{3+} was then measured by comparing the sums of the integrated intensities of all the Mn^{2+} EPR transitions with the sums of the integrated intensities of all the Fe^{3+} transitions (Chatelain and Weeks, 1973). The two sums were equal, within error. Hence the concentration of Fe^{3+} is ~2 percent of the total Fe concentration. If we assume that none of the Fe has entered into the formation of a second crystalline phase, *e.g.*, hematite and magnetite (Champness and Gay, 1968), then 98 percent of the Fe present in the crystal is divalent. This assumption is supported by the absence of any magnetic resonance components attributable to these phases, although they are observed after heating a sample in air to temperatures >500°C (Chatelain and Weeks, 1970).

The concentrations and variety of impurities in the Mn-doped crystal differ from those in the nominally pure crystal. Nonetheless, all of these, with the exception of sulfur, have concentrations $\leq 1/10$ the Mn concentration, which corresponds approximately to the amount of MnO added to the melt during crystal growth. We therefore assume that none of these impurities will have charge-transfer bands with absorption intensities of the same order of magnitude as those bands due to Mn^{2+}.

Experimental Procedure

Identification of those optical absorption bands in the nominally pure crystal which may be related to charge-transfer bands of Fe^{3+} is based on the effects of irradiation and heat treatments on the EPR spectrum of Fe^{3+} described by Chatelain and Weeks (1973). If some of the optical bands observed in this crystal can be shown to have the same dependence upon irradiation and subsequent heat treatments as was observed for the EPR spectrum of Fe^{3+}, a reasonable basis is established for relating these optical bands to electron transitions involving the Fe^{3+} ions. Hence the procedure by which this correlation was determined was a series of measurements of optical absorption and EPR spectrum of Fe^{3+} as a function of irradiation and heat treatments.

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[2] See "Note" immediately preceding "Conclusions."

Measurements of optical absorption in the range 0.75–5.0 eV were made at room temperature on a Cary Model 14 spectrophotometer. For these, a base line was established by measuring the "absorption" of the sample mask before mounting the sample. The data given in the figures are derived from the difference between the absorption before and after mounting the sample. A McPherson single-beam vacuum spectrometer was used for measurements at energies >5 eV. Optical absorption with and without the sample in the beam was measured at the peaks of the emission lines of the He-H discharge light source. Measurements at these energies provided an internal calibration of energy and a minimum in the ratio of stray background light to light transmitted by the sample. The stray-light background, constant throughout the range of energies over which measurements were made, was measured at 1000 Å with the sample in the beam and with only the sample mask in the beam. By measuring the background at 1000 Å, possible contributions from emission lines of the source were eliminated, since the LiF window through which light from the source passed effectively absorbs all photons with wavelengths <1050 Å.

Because of the weakly absorbing bands and the inhomogeneities at the core of the boule from which the samples were cut, the following steps were taken to minimize variations due to sample contamination or to changes in sample position in the beam. Surfaces upon which the source light was incident or from which it emerged were gently polished before each measurement and the position of the sample on the mask was fixed by forming a mold of Woods' metal on the mask into which the sample could be uniquely fitted.

The shape and size of the nominally pure crystal and the requirement for a maximum length for the light path through the crystal prevented an orientation such that the light path was parallel to any major crystal axis. The normal to the optical faces was perpendicular to the [010] direction and at an angle of 25° to the [001] direction. In this orientation the optical path was 0.3 cm. Since it was necessary to minimize path length in the Mn-doped crystal, these constraints on orientation were removed and the incident light was normal to a (010) plane.

TABLE 1. Impurities in Synthetic Mg_2SiO_4 Crystals

Crystal Impurity	Nominally Pure*	Doped with 0.1 wt % MnO*
Al	20	5
As	2	
Ca	40	70
Co	5	< 0.3
Cr	0.5	30
Cu	30	6
Fe	50	100
K	4	7
Mn	2	900
Na	20	1
Ni	8	30
Pb	4	N.D.
Zn	8	4
Mo		20
Ti		< 8
S		400

*ppm by weight ± 50 percent.

A homodyne EPR spectrometer operating at ~9 GHz and room temperature was used to record the spectrum of the nominally pure crystal. The spectrum was recorded for only one crystal orientation with respect to the applied magnetic field, **H**, *i.e.*, **H** parallel to the *c* [001] axis. Intensities of three lines of the Fe^{3+} spectrum were carefully measured before and after each treatment. The spectrum of Mn^{2+} was also observed in the spectra of the as-received (untreated) crystal. Since no change in this spectrum was observed as a result of the various treatments, it was used as an internal standard for intensity measurements of the Fe^{3+} lines. The error in the intensity measurements is ±20 percent.

The nominally pure crystal was irradiated in air at ~30°C in a ^{137}Cs source for 3 hours (~10^6R hr^{-1}) and subsequently heated in air to various temperatures in a furnace whose temperature was controlled to ±1°C.

Experimental Results and Discussion

The absorption spectrum of the nominally pure crystal before and after irradiation with 6.4×10^{15} photons cm^{-2} [$E(^{137}Cs\ \gamma) = 0.663$ MeV] is shown in the upper part of Figure 1. The difference, $\Delta\alpha$, between these two curves is plotted in the lower part. Before irradiation, peaks in the absorption are resolved at 4.65, 6.00, and 6.30 eV. A shoulder on the absorption curve at 3.5 eV is probably due to a fourth peak. Above 6.5 eV, the absorption increases rapidly, exceeding the range of the spectrometer at ~7.25 eV.

After irradiation, the absorption decreased between 0.75 and 2 eV, increased between 2.25 eV and 4.0 eV, and decreased between 5.0 and 7.20 eV. The lower part of Figure 1, in which $\Delta\alpha$ is plotted, shows more clearly the effect of irradiation on the

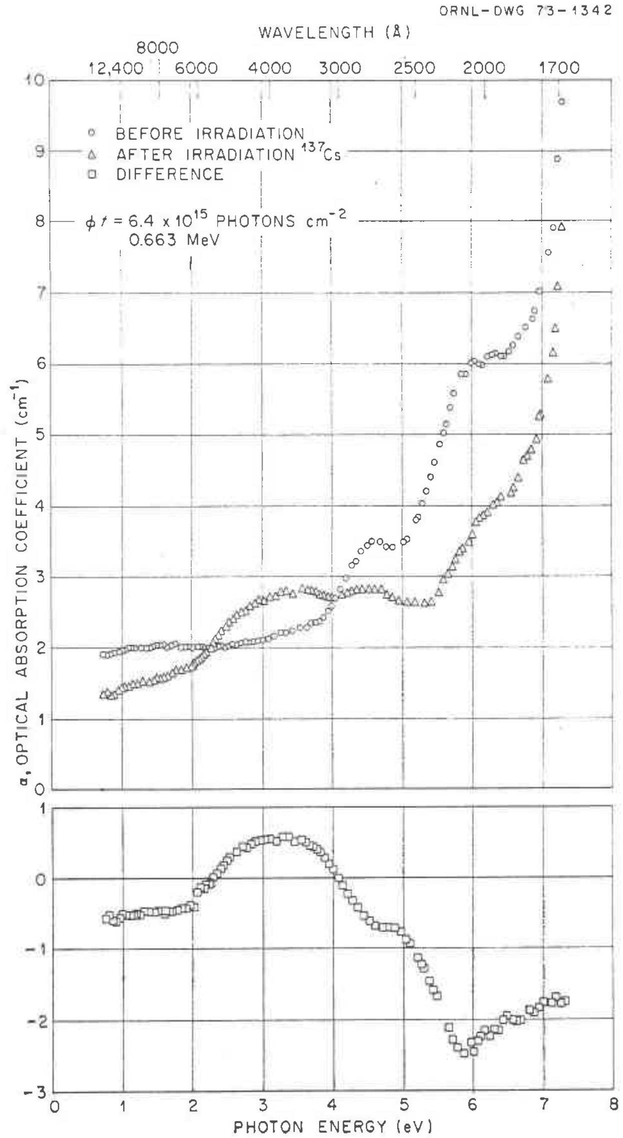

FIG. 1. Optical absorption as a function of energy in a nominally pure synthetic Mg_2SiO_4 single crystal. The sample was irradiated with ^{137}Cs gamma rays at ~30°C.

spectrum. At least two bands at 2.75 and 3.35 eV were induced by the irradiation, while bands at 4.75, 6.00, and 6.50 decreased in intensity. Between 6.65 and 7.25 eV, there is probably a fourth band which also decreased. The largest decrease occurred in the 6.00 eV band.

Upon heating the sample at 100, 150, 250, and 300°C, the absorption spectrum returned to approximately its initial form. This recovery is plotted in Figure 2 as a "fraction of damage" remaining after each heat treatment at 2.76, 3.54, and 6.24 eV. Also plotted in the same way are data on one of the Fe^{3+} EPR lines. The intensity of this line after irradiation was reduced to ~0.2 the initial intensity. (All the other EPR lines of the Fe^{3+} spectrum behaved in an identical fashion.) A comparison of the curves for optical absorption at the three energies with the curve for the EPR line shows that the correspondence between the absorption at 6.24 eV and the EPR line is excellent. With irradiation, the decrease in absorption at 6.24 eV also corresponds to a decrease in intensity of the Fe^{3+} EPR lines. Hence, on the basis of the congruence in the curves in Figure 2 and the concurrent decrease and increase in intensity of optical absorption and EPR line intensity, we attribute a major fraction of the absorption at 6.24 eV to electron transitions involving the Fe^{3+} ions in the lattice. A similar congruence was found for the 6.0 and 6.50 energies.

From Figure 1 (upper part), we estimate that approximately one-third of the absorption at 6.24 eV is attributable to Fe^{3+}. The remaining absorption is

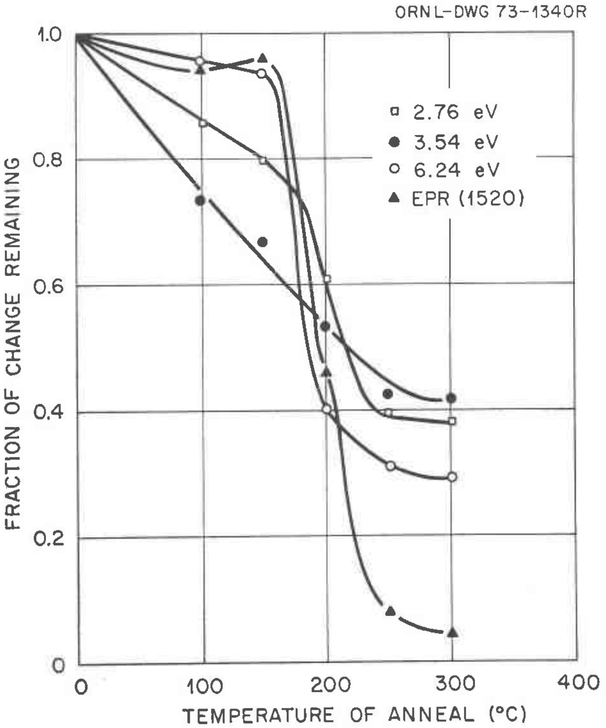

FIG. 2. Fractional change in optical absorption at three energies and the intensity of one of the Fe^{3+} EPR lines after annealing for 3 minutes at the indicated temperatures. The number in parentheses following the symbol for the EPR data is the magnetic field at which the EPR transition occurred. The curves are drawn through the data points.

due to the other impurities present in the crystal. Because of the great variety of impurities present in the crystals and the occurrence after irradiation of absorption bands in this energy range in silicate compounds containing similar concentrations of such impurities (Lell, Kreidl, and Hensler, 1966), we attribute the increase in absorption between 2 and 4 eV to alterations of the valence states of some of these impurities.

From the $\Delta\alpha$ curve the change in the 6.00 eV absorption is $\Delta\alpha = -2$, if we assume that the base line is at $\Delta\alpha = -0.5$. This difference curve has a width, ΔE, at half-maximum amplitude of ~ 1 eV in the region of 6.0 eV. We assume this width to be the width of the absorption band due to Fe^{3+}. An estimate of the concentration, η, of Fe^{3+} ions (10^{16} cm^{-3}) has been given above. Using these estimates, an oscillator strength can now be calculated for the absorption band attributed to Fe^{3+} by the relation

$$f = \frac{7 \times 10^{15} \alpha_{max}\, \Delta E}{\eta},$$

giving $f \sim 1$ where only the Lorentz local field correction is applied and the band shape is assumed to be Gaussian (Dexter, 1958).

The optical absorption coefficient of the Mn-doped crystal is plotted in Figure 3. For purpose of comparison, the absorption coefficient of the nominally pure crystal is also shown. The absorption of the Mn-doped crystal between 0.75 and 4.0 eV is small and approximately constant. It then rises to a peak at 4.75 eV and at energies >5 eV rises sharply to a shoulder at 6.3 eV and exceeds instrument range at energies >7.2 eV. The absorption coefficient of the nominally pure crystal has a small increase at energies >5 eV, and at energies ≥7.25 eV a rapid increase begins. Comparison of the two curves reveals the Mn-doped crystal to have two strong absorption bands at 6.5 and >7.25 eV, both with energies less than those due to transitions associated with the primary ions of the crystal, Mg, Si, and O. Since Mn is at least an order of magnitude more abundant than any other impurity in the Mn-doped crystal, with exception of S, we attribute these two bands to transitions involving Mn.

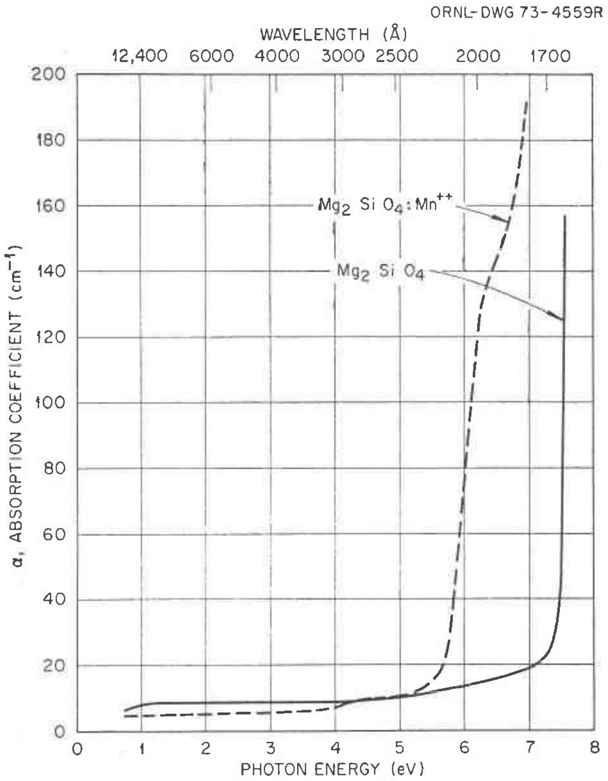

FIG. 3. Optical absorption as a function of energy for a thin sample of nominally pure Mg_2SiO_4 crystal doped with 0.1 wt percent MnO. The two curves replace the data points.

The oscillator strength of the 6.5 eV transition is $f \sim 0.1$, assuming that $\Delta E = 1$ eV $\alpha_{max} = 140$, and $\eta = 10^{19}$ cm^{-3}. An estimate of f for the >7.25 eV band is more difficult, since the peak of this band is not resolved and hence a value for α_{max} cannot be obtained. A careful examination of the data points between 6.85 eV and the last point at 7.10 eV shows that $d\alpha/dE$ has a maximum at 7.00 eV which may be due to the low energy-inflection point of the >7.25 eV band. If this is a correct interpretation of the inflection point at 7.00 eV, and we assume that $\Delta E \approx 1.0$ eV for this band, that the peak is at ~ 7.5 eV, and that $\alpha_m \sim 2\alpha$ (inflection point) ~ 400, then $f \sim 0.3$. These oscillator strengths are of the magnitude expected for charge-transfer transitions. Hence it will be useful to estimate the energies expected for these transitions for Fe^{3+} and Mn^{2+} in Mg_2SiO_4.

For the purposes of this estimate, we assume that the ions are substitutional for Mg only at $[M(2)]^3$, one of the two possible Mg sites (Chatelain and Weeks, 1970, 1973). The oxygen-coordination polyhedron about the $M(2)^3$ site is not a regular figure, but its local symmetry is approximately $3m(C_{3v})$ with the triad axis parallel to a (Burns, 1970). Although the site is distorted, the crystal field terms

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[3] See "Note" immediately preceding "Conclusions."

obtained from EPR data (Chatelain and Weeks, 1970, 1973) show that the distortion is not sufficient to alter the high-spin state of Fe^{3+}. The magnitudes of the crystal-field terms for Mn^{2+} are less than those for Fe^{3+} (Chatelain and Weeks, 1970, 1973). As a first approximation, the crystal electric field is that of a slightly distorted octahedral array of oxygen ions and is similar to that of Al_2O_3 (Ballhausen, 1962). However, since the valence of the Al ion differs by one from that of the Mg ion, the charge-transfer processes will be considered relative to MgO rather than to Al_2O_3.

For the host structure the charge-transfer process gives

$$O^{=}(2p^6) + Si^{4+}(2p^6) \rightarrow O^{-}(2p^5) + Si^{3+}(2p^6 3s)$$

and

$$O^{=}(2p^6) + Mg^{2+}(2p^6) \rightarrow O^{-}(2p^5) + Mg^{+}(2p^6 3s)$$

in an extreme tight-binding model for the interband transitions. Optical absorption of nominally pure SiO_2 (α-quartz), MgO, and Mg_2SiO_4 have been measured, and the first intense absorption in the three materials occurs at energies >7.5 eV (Weeks, 1970; Roessler and Walker, 1967; Williams and Arakawa, 1967; Shankland, 1968). The point symmetry of the Si site and the Si-O distances in Mg_2SiO_4 are approximately the same as in α-quartz SiO_2, and hence the O → Si charge-transfer energy is expected to be approximately equal for the two crystals, *i.e.*, ≥ 8.5 eV. The $M(1)$ and $M(2)$ sites occupied by Mg in Mg_2SiO_4 are distorted octahedra, whereas the Mg site in MgO is a regular octahedron. Consequently, some difference in the energy of the O-Mg charge-transfer transition in MgO and Mg_2SiO_4 is expected. As the data in Figure 2 show, the optical absorption of the nominally pure crystal displays a rapid increase in α at energies >7.3 eV. Shankland (1968) has observed a similar absorption in other synthetic Mg_2SiO_4 crystals. This rapid increase is probably due to the charge-transfer absorption O → Mg, since the energy is approximately the same at the O → Mg absorption in MgO (Roessler and Walker, 1967; Williams and Arakawa, 1967). Hence any absorption bands at energies <7.3 eV are due to impurities, *e.g.*, Fe^{3+} and Mn^{2+}.

The energy of the first charge-transfer transition for these two ions, assuming that they are located in an $M(2)$ site, is (Tippens, 1970; Modine, 1971)

$$E_{ct} = E_x - [I(Fe^{2+}) - I(Mg^{+})] + V_s + \frac{e^2}{r} + V_P$$

and

$$E_{ct} = E_x - [I(Mn^{+}) - I(Mg^{+})] + V_s$$

where E_x is the exciton energy, I is the ionization energy of the respective ions, V_s is the d-shell stabilization energy, e^2/r is the binding energy of the exciton, and V_p is the polarization energy due to the excess charge on the Fe^{3+} ion. In MgO the Mg–O distance is 2.105 Å (Bragg, Claringbull, and Taylor, 1965) and in the $M(2)$ site of Mg_2SiO_4 the Mg–O distances are between 2.07 and 2.17 Å (Bragg *et al*, 1965). Thus the average Mg–O distance in the $M(2)$ site is approximately the same as the Mg–O distance in MgO. Similarly, the static dielectric constants of the two crystals are only slightly different. It is, therefore, reasonable to assume that the $M(2)$ site in Mg_2SiO_4 will have exciton energies, exciton binding energies, and polarization energies for Fe^{3+} that do not differ greatly from those for MgO. The lower symmetry of the $M(2)$ site in Mg_2SiO_4 compared with the cubic symmetry of Mg in MgO will have some effect on these energies. For purposes of establishing the approximate energy of the first charge-transfer band of Fe^{3+}, these approximations are sufficient. Using the value for V_p estimated by Modine (Modine, 1971) on the basis of the continuum model, $V_p = 6.2$ eV, and a value for the exciton energy of MgO, $E_x = 7.6$ eV (Reiling and Hensley, 1958), assuming that the first charge-transfer is to a t_{2g} orbital so that $V_s = -4\,Dq \sim -0.8$ eV (Tippens, 1970), $I(Fe^{2+}) - I(Mg^{+}) = -15.4$ eV (Griffiths, 1961), and $e^2/r = 6.9$ eV, then $E_{ct}(Fe^{3+}) \approx 4.5$ eV. On the other hand, if the exciton band is at 8.4 eV as suggested by Shankland (1968), then $E_{ct}(Fe^{3+}) \approx 5.3$ eV. For Mn^{2+}, $V_p = 0$, $e^2/r = 0$, $I(Mn^{+}) - I(Mg^{+}) = 0.5$ eV (Griffiths, 1961), $V_s = -4\,Dq \approx -0.4$ eV (Ballhausen, 1962), and hence $E_{ct} \approx 6.7$ eV. These values are compared with the energies of the transitions attributed to Fe^{3+} and Mn^{2+} in Table 2. The agreement between the estimated value of the lowest energy E_{ct} and the lowest energy peak due to Mn^{2+} is quite good. The energy of the next transition also has a value within the range expected (Tippens, 1970). In the case of the Fe^{3+} transitions, a band is observed at 4.7 eV in the unirradiated crystal which decreases in intensity with irradiation corresponding approximately to the decreases observed at 6.0 and 6.0 eV. However, due to other weak absorption bands in the region of 4.7 eV, the correlation between the 6.0 eV band and the EPR spectrum as a function of heat treatments (Fig.

2) has not been established for the 4.7 eV band. The ratios of the intensities of the 4.7, 6.0, and 6.6 eV bands in the spectrum of the Mg_2SiO_4 crystal do correspond approximately to the intensity ratios of the three Fe^{3+} charge-transfer bands in the spectrum of Al_2O_3 (Tippens, 1970). Hence it is assumed that the lowest-energy charge-transfer band of Fe^{3+} in Mg_2SiO_4 is the 4.7 eV band. In MgO the lowest-energy band is at 4.3 eV, while the next two bands are probably at 6.2 and 6.7 eV (Lehmann, 1971).

If it is assumed that the 4.7 eV band and the 6.0 eV band of the Fe^{3+} spectrum are spin-allowed transitions between $t_{1u}(\pi)$ and $t_{2g}(\pi^*)$ and between $t_{1u}(\pi)$ and $e_g(\sigma^*)$ (Modine, 1973), respectively, then the crystal-electric-field splitting of these states, Dq, is equal to the difference in energies and hence $10\,Dq \approx 1.3$ eV or $Dq = 0.13$ eV $= 1050$ cm^{-1}. If a similar assumption is made for the 6.5 and ~7.5 eV bands of Mn^{2+}, then $Dq \approx 800$ cm^{-1}.

In the case of the Fe^{3+} transitions, there are other possible combinations of the initial and final states. It may be that the 6.0 eV band is a $t_{1u}(\pi)$ to $t_{2g}(\pi^*)$ transition and the 6.6 eV band the $t_{2u}(\pi)$ to $e_g(\sigma^*)$ transition. In this case $Dq \approx 1500$ cm^{-1}. This value for Dq is the same as the value for Fe^{3+}:Al_2O_3 (Krebs and Maisch, 1971; Lehmann and Harder, 1970) and less than the value found for Fe^{3+} in octahedral sites in garnet, for which $Dq \approx 1260$ cm^{-1} (Moore and White, 1972). The smaller value of Dq, 1050 cm^{-1}, is consistent (Orgel, 1957) with the larger metal-oxygen distance in Mg_2SiO_4 (Gibbs, 1963) as compared with the distance in Al_2O_3 (Pauling and Hendricks, 1925). This value is also less than that found for Fe^{3+} in octahedral crystal electric fields of various other oxides (Lehmann and Harder, 1970; Wood and Remeika, 1967). Corresponding data for Mn^{2+} charge-transfer spectra are scarce. However, $Dq = 850$ cm^{-1} for Mn in the octahedral field of six H_2O molecules (Ballhausen, 1962), a value in close agreement with the estimate of Dq given above. This estimate is also less than the value of Dq for Fe^{3+}, a result consistent with the EPR data.

Note

In a private communication, S. Zeira and S. S. Hafner describe EPR measurements on Fe^{3+} in synthetic crystals in which Fe^{3+} occupies both $M(1)$ and $M(2)$ sites. Their EPR parameters for Fe^{3+} in the site they identify as $M(1)$ agree with those measured by Chatelain and Weeks (1973) in the crystals used for these experiments. Because of better resolution in their measurements, they are able to distinguish between Fe^{3+} in $M(1)$ sites and in $M(2)$ sites. On the basis of their measurements, Fe^{3+} in our crystals should be assigned to $M(1)$ sites. The arguments presented here are not altered by assigning Fe^{3+} to the $M(1)$ site.

TABLE 2. Energies of Charge-Transfer Transitions of Fe^{3+} and Mn^{2+} in Mg_2SiO_4

Ion	E_{ct} (estimate)	E_{ct} (observed)	f*	E_{ct}** (Al_2O_3)
Fe^{3+}	4.5[†]	4.7 (?)	0.2 (?)	4.78
	6.3[††]	6.0	1	6.38
		6.6	0.5	7.2
Mn^{2+}	6.3	6.5	0.1	
		∿ 7.5	0.3	

*This estimate of oscillator strength is an order of magnitude estimate.

**H. H. Tippens, Phys. Rev. B, 1, 126 (1970).

[†] This value is in agreement with observations on the first charge-transfer band of Fe^{3+} in MgO (see Ref. Soshea et al.), but if the exciton band is at 8.4 eV, then the estimated value is 5.3 eV.

[††] The second charge-transfer band should be ≈ 10 Dq above the first band and for MgO a second band is observed at 6.2 eV (see Ref. 10).

Conclusions

The alterations of three optical absorption bands of nominally pure Mg_2SiO_4 single crystals by irradiation with ^{137}Cs gamma rays and subsequent thermal treatments are correlated with alterations of the EPR spectrum of Fe^{3+}. On the basis of this correlation, these bands have been attributed to optical transitions associated with the Fe^{3+} ion. An estimate of the oscillator strengths of the bands, determined from the concentrations of Fe^{3+} ions, is of a magnitude expected for electric-dipole-allowed transitions. It is assumed that these transitions are of this nature, and thus are attributed to ligand-ion charge-transfer transitions. Estimates of the magnitude of the crystal-field splitting, Dq, for Fe^{3+} and Mn^{2+}, derived from the energy differences of the optical bands, are in reasonable agreement with the magnitude of Dq for these ions in other oxide compounds in which these ions occupy octahedral crystal sites.

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