

## DETERMINATION OF THE DISTRIBUTION OF TRACE AMOUNTS OF Mn<sup>2+</sup> IN DIOPSIDES BY ELECTRON PARAMAGNETIC RESONANCE

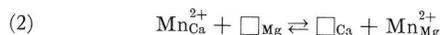
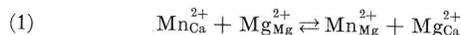
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### ABSTRACT

The electron paramagnetic resonance of Mn<sup>2+</sup> in diopside shows that Mn<sup>2+</sup> occurs in two different lattice sites. The spin Hamiltonian parameters of Mn<sup>2+</sup> in diopside determined by Vinokurov, Zaripov and Stepanov (1964) have been confirmed. However, their site assignment has been reversed with the known distortion of the CaO<sub>8</sub> and MgO<sub>6</sub> coordination polyhedra, namely, the Mn<sup>2+</sup> EPR spectrum showing the larger 'D' and smaller 'A' parameters has been assigned to the more distorted Ca-site.

Three types of Mn<sup>2+</sup> distribution have been found in natural diopsides: (1) most Mn<sup>2+</sup> in the Ca-site, (2) most Mn<sup>2+</sup> in the Mg-site, and (3) all Mn<sup>2+</sup> in the Mg-site. Natural and synthetic diopsides known to have crystallized above 900°C and containing ~ 0.001% Mn or less invariably show all Mn<sup>2+</sup> in the Mg-site. A Californian diopside (Y6), with Mn concentration 0.005% and 76% Mn<sup>2+</sup> in Ca-site has been heat-treated to induce a redistribution of Mn<sup>2+</sup> in the Ca and Mg-sites. The exchange begins at 900°C and is essentially complete at 1050°C, at which point the Mn<sup>2+</sup> distribution is reversed, with 85% of the Mn<sup>2+</sup> in the Mg-site. Two possible exchange reactions are suggested:



the subscripts denoting Ca- and Mg-sites and  $\square$  denoting a vacancy.

### INTRODUCTION

Ions of the 3d transition metals occur in various silicates in concentrations varying from parts per million to almost complete replacement of other cations. Cation distribution investigations with X-ray diffraction and Mössbauer techniques show that many of these minerals have ordered arrangements between transition metal ions and other cations. However, these techniques require relatively high concentrations of the particular ions investigated. The present paper reports preliminary measurements of the distribution of Mn<sup>2+</sup> in the Ca- and Mg-sites of some diopsides by electron paramagnetic resonance, where manganese concentration is less than one percent. A brief report of this work has already appeared (Ghose, Schindler, and Hafner, 1968).

### CRYSTALLOGRAPHY

The structure of diopside, CaMgSi<sub>2</sub>O<sub>6</sub>, determined by Warren and Bragg (1928), is typical of pyroxenes crystallizing in the space group C2/c. A careful refinement of the structure has been carried out recently by Clark, Appleman and Papike (1968). The structure (Fig. 1) consists of single SiO<sub>3</sub> chains running parallel to *c*, held together by polyhedral sheets made up of CaO<sub>8</sub> polyhedra and MgO<sub>6</sub> octahedra. There are two crystallographically different polyhedral cation sites other than the tetrahedral Si-sites, which can be termed M1 = Mg-site and M2 = Ca-site to be able to compare them

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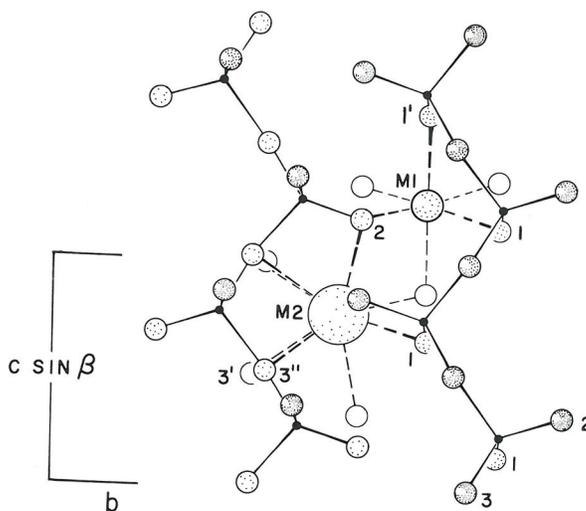


FIG. 1. Crystal structure of diopside, CaMgSi<sub>2</sub>O<sub>6</sub>, viewed along the *a* axis (from Clark, Appleman, and Papike, 1968). M1 = Mg, M2 = Ca.

with similar cation sites in other pyroxene structures.

Diopside is monoclinic, with *a* = 9.478, *b* = 8.924, *c* = 5.251 Å and β = 105°40'. There are 4 Ca and 4 Mg atoms in the unit cell, occupying positions of the type ±(0, *y*, ¼), with *y*<sub>Ca</sub> = 0.3015 and *y*<sub>Mg</sub> = 0.9082. The point symmetry of these sites is 2, the symmetry axis coinciding with the crystallographic *b* axis. The 4 Ca (likewise 4 Mg) positions in the unit cell are related in pairs through centers of inversion and are not magnetically distinguishable. Hence, for any orientation of the crystal

TABLE 1. INTERATOMIC DISTANCES WITHIN THE  $\text{Ca-O}_8$  POLYHEDRON AND  $\text{MgO}_6$  OCTAHEDRON IN DIOPSIDE (AFTER CLARK, APPLEMAN, AND PAPIKE, 1968)<sup>a</sup>

Atoms	Distances <sup>b</sup> (Å)
Ca-O1	2.360±1
Ca-O2	2.353±3
Ca-O3'	2.561±2
Ca-O3''	2.717±1
Mg-O1	2.115±1
Mg-O1'	2.065±3
Mg-O2	2.050±2

<sup>a</sup> See Fig. 1.

<sup>b</sup> Each distance occurs twice.

within the magnetic field, only two sets of  $\text{Mn}^{2+}$  spectra, one each from  $\text{Mn}^{2+}$  in the Ca- and Mg-sites, are observed.

The Ca-O and Mg-O bond distances are listed in Table 1. The  $\text{MgO}_6$  octahedron is nearly regular with an average Mg-O bond distance of 2.08 Å, the maximum deviation from this value being + 0.04 Å. The  $\text{CaO}_8$  polyhedron in contrast is highly distorted with an average Ca-O bond distance of 2.50 Å, the maximum deviation being as large as + 0.22 Å. In johannsenite,  $\text{CaMnSi}_2\text{O}_6$  the situation is very similar (Freed and Peacor, 1967). In this mineral the average Ca-O bond distance is 2.53 Å, the maximum deviation being + 0.24 Å, while the average Mn-O bond distance is 2.17 Å, the maximum deviation being + 0.06 Å. It is clear that a complete substitution of Mg by Mn in the *M*1 site of the diopside structure does not distort the *M*1-octahedron to any great extent. Vinokurov, Zaripov and Stepanov (1964) have come to the opposite conclusion regarding the relative distortion of the  $\text{CaO}_8$  and  $\text{MgO}_6$  coordination polyhedra. They consider two out of the eight oxygens belonging to the  $\text{CaO}_8$  polyhedron to be "inactive" and the Ca-O polyhedron therefore to be essentially an octahedron, which is more regular than the  $\text{MgO}_6$  octahedron. Even if we neglect the two longest Ca-O bonds (= 2.75 Å), the refined bond distances (Clark, Appleman and Papike, 1968) indicate that the  $\text{CaO}_6$  "octahedron" is definitely more distorted than the  $\text{MgO}_6$  octahedron (see Table 1).

#### ELECTRON PARAMAGNETIC RESONANCE: THEORY

The electronic paramagnetism of the  $\text{Mn}^{2+}$  ion is due to the 5 unpaired electrons in the 3*d* shell. The effective electronic spin *S* of the ion is 5/2. In spectroscopic nomenclature, it is a  $^6S_{5/2}$  state. In the EPR experiments, this state is split by three different interactions: (1) with the crystalline electric field (crystal field or Stark interaction); (2) with the applied magnetic field (Zeeman interaction); (3) with the magnetic moment of the  $^{55}\text{Mn}$  nucleus (hyperfine interaction).

The crystalline electric field splits the six-fold degenerate ground state into three two-fold degenerate levels. These

levels are labelled by the spin quantum numbers,  $m_s = \pm 5/2, \pm 3/2$  and  $\pm 1/2$ . The magnetic field further splits these into levels labeled + 5/2 and - 5/2 etc. Each of the six levels is further split by the interaction of the electronic spin with the nuclear spin  $I = 5/2$  of the  $^{55}\text{Mn}$  nucleus into six sublevels. Thus a total of thirty-six levels will be present for a system with  $S = 5/2$  and  $I = 5/2$ . An energy level diagram for such a system is given in Figure 2, together with some of the transitions. According to the selection rules, these transitions occur between levels differing by one in the electronic spin quantum number ( $\Delta m_s = 1$ ) and not differing in the nuclear spin quantum number ( $\Delta m_I = 0$ ).

The Hamiltonian operator describing the energy of the system, known as the spin Hamiltonian, is given by:

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + \mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S} + \mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I} + g_N\beta_N\mathbf{H}\cdot\mathbf{I} + \mathbf{I}\cdot\mathbf{Q}\cdot\mathbf{I}$$

where

- g** = spectroscopic splitting tensor
- $g_N$  = nuclear *g*-factor
- β** = Bohr magneton
- $\beta_N$  = nuclear magneton
- H** = applied magnetic field
- D** = crystal-field interaction tensor
- A** = hyperfine interaction tensor
- Q** = nuclear electric quadrupole interaction tensor

The first three terms are the electron Zeeman, Stark and the hyperfine terms. The fourth term describes the interaction of the nuclear spin with the applied magnetic field, **H**. The last term describes the interaction of the nuclear electric quadrupole moment with the crystalline electric field gradient at the nucleus. These two latter interactions do not split the energy levels any further, but shift them somewhat. The transitions are however affected by these interactions only in the second order.

An experimental spectrum, as observed in the Y6 diopside, is shown in Figure 3. There are clearly five groups of six lines each; superimposed on the central group there is a second set of six lines with different amplitude and different splitting plus a small line in the center. This second set is also part of a thirty line spectrum, but the outside groups can be observed only at higher spectrometer gain. The small central line has not been investigated, but is due to some other impurity in the crystal.

It is apparent that the amplitude of the two groups are significantly different. When the lines are narrow (half width ~ 1 G), as in the diopside Y6, integration techniques allow fairly good estimates of the relative numbers of spins contributing to each of the two resonances (error limit ± 5%). If the lines are much wider (half width ~ 10 G), the lines from two different sets will overlap and estimates of the relative concentrations will be much less accurate. A difficulty encountered only with the

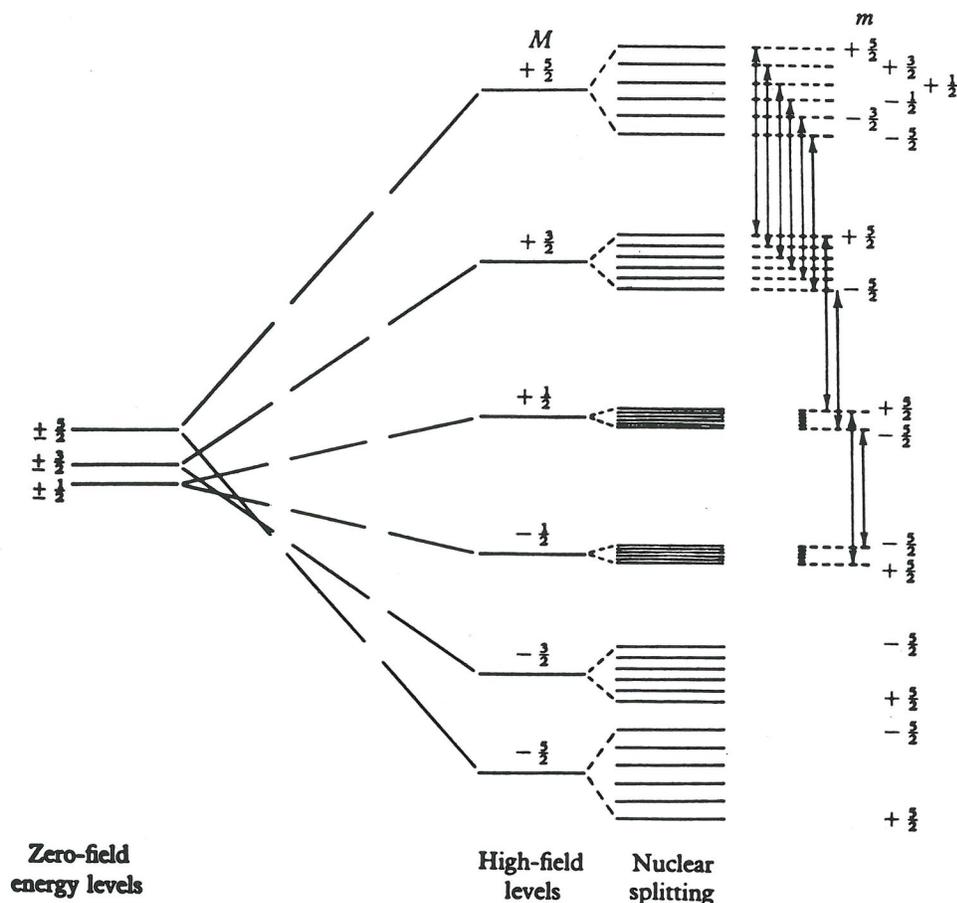


FIG. 2. A schematic energy-level diagram for the  $Mn^{2+}$  ion showing the electronic levels in zero and in strong magnetic field together with the splitting due to the nuclear spin. Some of the typical transitions are indicated by arrows (from Bleany and Ingram, 1951).

diopside Y6 is that the absorption lines from one set of  $Mn^{2+}$  saturate differently from the lines of the other set. Care has to be taken to operate at power level low enough to avoid saturation of either of the two systems.

#### EXPERIMENTAL

All EPR spectra were taken on a Varian V-4503 spectrometer operating at 35 GHz. The Fieldial field control unit was calibrated with a proton Gaussmeter and the microwave frequency was determined with the built-in wavemeter. The crystals ( $\sim 1$  mm in diameter) were mounted on quartz or lucite rods glued to the bottom of the cylindrical  $TE_{011}$  cavity. To prevent saturation of either set of lines, measurements were made at the highest power level at which a change in power of 3 db in either direction would not result in a change in the relative intensities of the lines in question. All spectra were taken at ambient temperature. Intensities were obtained from calculations of the first moment of the observed first derivative absorption lines. In the course of the present work, a large number of diopside samples was examined. To insure reproducible results, all quantitative measurements were taken with the

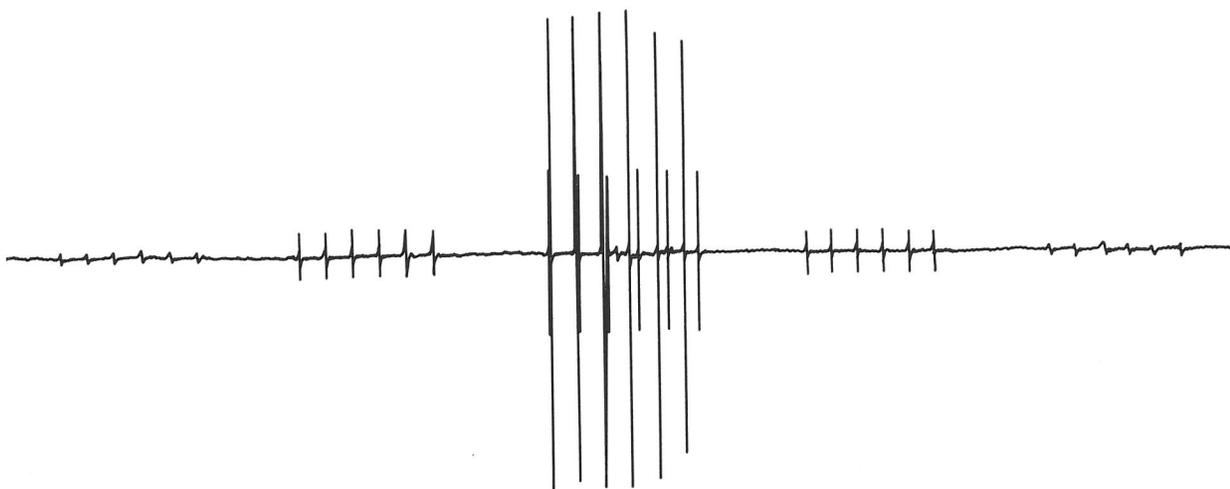
magnetic field oriented along one of the magnetic axes of the centers, as this resulted in the best separation of the lines and in the absence of all forbidden transitions. The heating experiments were performed in sealed evacuated quartz tubes. After heating for periods of 24 to 72 hours, the samples were quenched in water to room temperature.

#### SPIN HAMILTONIAN PARAMETERS AND SITE ASSIGNMENT

Vinokurov, Zaripov and Stepanov (1964) have carefully determined the spin Hamiltonian parameters of  $Mn^{2+}$  in diopside. They have used the spin-Hamiltonian of the form:

$$\begin{aligned} \mathcal{H} = & g_z \beta H_z S_z + g_x \beta H_x S_x + g_y \beta H_y S_y \\ & + 1/3 b_2^0 O_2^0 + 1/3 b_2^2 O_2^2 \\ & + 1/60 b_4^0 O_4^0 + 1/60 b_4^2 O_4^2 + 1/60 b_4^4 O_4^4 \\ & + A S_z I_z + B S_x I_x + C S_y I_y \end{aligned}$$

to describe the spectrum. The form of the operators  $O_m^n$  is given by Orbach (1961). The term  $b_2^0$  corresponds to the

FIG. 3.  $\text{Mn}^{2+}$  EPR spectrum of diopside, Y6.

crystal field parameter  $D$ , which essentially determines the degree of axial distortion of the crystalline electric field from a regular cubic symmetry. If the crystal field is orthorhombic, which is the case for diopside, two other constants  $b_2^2$  and  $b_4^2$  are necessary to describe the crystal field interaction. We have essentially confirmed these parameters (Ghose, Schindler and Hafner, 1968).

The assignment of the two sets of  $\text{Mn}^{2+}$  spectra to the Ca- and Mg-sites in the diopside structure is based on the measured spin Hamiltonian parameters (Table 2). The spectrum with the larger  $b_2^2$  ( $= D$ ) and smaller  $A$  parameters has been assigned to  $\text{Mn}^{2+}$  in the Ca-site, while the spectrum with the smaller  $D$  and larger  $A$  values has been assigned to  $\text{Mn}^{2+}$  in the Mg-site. This site-assignment is reverse of that made by Vinokurov, Zaripov and Stepanov (1964). For  $\text{Mn}^{2+}$  in the Mg-site, the "rhombic" constants

$b_2^2$  and  $b_4^2$  are respectively 6 and 2 times smaller, while the "cubic" constants  $b_4^0$  and  $b_4^4$  are respectively 20 and 2 times greater than for  $\text{Mn}^{2+}$  in the Ca-position. This indicates that the crystalline electric field of the nearest neighbors for the  $\text{Mn}^{2+}$  ion in the Mg-position is more symmetrical than that in the Ca-position, which is consistent with the recent structure refinement of diopside.

The hyperfine splitting parameter  $A$  is smaller for  $\text{Mn}^{2+}$  in the Ca-site than for  $\text{Mn}^{2+}$  in the Mg-site, which indicates a greater degree of covalency of the Mn-O bond for  $\text{Mn}^{2+}$  in the Ca-site. Matumura (1958) has presented a linear relationship between the hyperfine splitting parameter  $A$  and the ionicity calculated after Pauling (1940). From this relationship and the measured  $A$  parameters, the ionicities of the Mn-O bond for  $\text{Mn}^{2+}$  in the Ca- and Mg-sites have been determined to be 88 percent and 91.5 percent respectively. It is interesting to note that the slightly smaller Mössbauer isomer shift of  $\text{Fe}^{2+}$  in the  $M2$  site in orthopyroxenes indicates that Fe is somewhat more covalently bonded at this site than at  $M1$  (Evans, Ghose, and Hafner, 1967). Thus,  $M1$  and  $M2$  sites in both clino- and ortho-pyroxenes seem to show the same trend so far as the relative covalency is concerned.

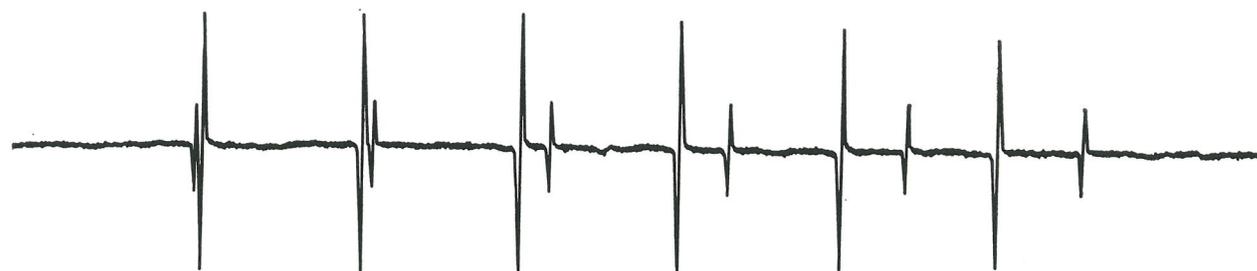
In the following analysis, the identification of the  $\text{Mn}^{2+}$  EPR spectra in natural diopsides is based on the hyperfine splitting (hfs) of the central part of the spectrum consisting of two six-line patterns corresponding to  $m = +\frac{1}{2} \rightarrow m = -\frac{1}{2}$  transition. Thus, according to our assignment, the spectrum showing the larger hfs belongs to  $\text{Mn}^{2+}$  in the Ca-site.

## RESULTS

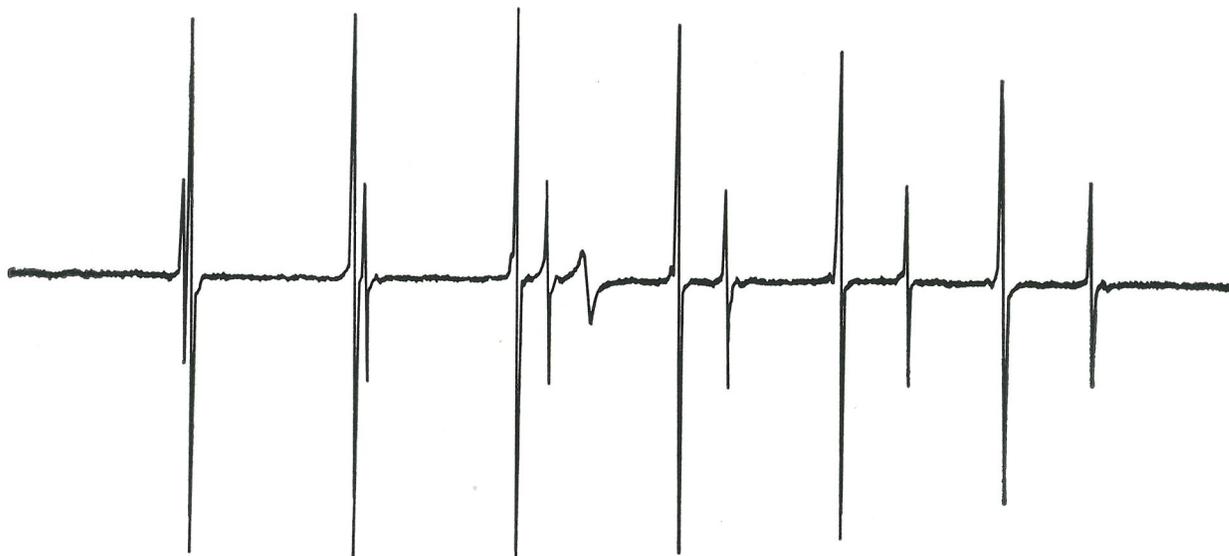
The diopside sample, Y6, occurs in a contact metamorphic rock from the Twin Lakes region, Fresno County, California (Chesterman, 1942), and is unusually pure,

TABLE 2. SPIN HAMILTONIAN PARAMETERS OF  $\text{Mn}^{2+}$  IN DIOPSIDE (FROM VINOKUROV, ZARIPOV, AND STEPANOV, 1964; SITE ASSIGNMENT BY GHOSE, SCHINDLER AND HAFNER, 1968) IN GAUSS, EXCEPT  $g$

Parameters	Ca-Site	Mg-Site
$g_z$	$2.0017 \pm 5$	$2.0015 \pm 5$
$g_x$	$2.0016 \pm 8$	$2.0013 \pm 8$
$g_y$	$2.0016 \pm 8$	$2.0008 \pm 8$
$A$	$84.4 \pm 0.5$	$91.3 \pm 0.5$
$B$	$84.4 \pm 0.5$	$91.7 \pm 0.5$
$C$	$81.9 \pm 0.5$	$90.8 \pm 0.5$
$b_2^0$ ( $\equiv D$ )	432.95	373.84
$b_2^2$	-308.5	51.26
$b_4^0$	0.34	-6.58
$b_4^2$	-4.74	-2.93
$b_4^4$	15.88	32.47



(a) Unheated



(b) Heated at 900°C



(c) Heated at 1100°C

FIG. 4.  $Mn^{2+}$  EPR spectra of diopside Y6 ( $m = +\frac{1}{2} \rightarrow m = -\frac{1}{2}$ ), unheated and heated to 900°C and 1100°C.

TABLE 3. FRACTIONS OF  $Mn^{2+}$  IN CA- AND MG-SITES OF DIOPSIDE, Y6, AS A FUNCTION OF TEMPERATURE<sup>a</sup>

Temperature, °C	Fraction of $Mn^{2+}$ in	
	Ca-Site	Mg-Site
Unheated	0.76	0.24
900°	.74	.26
950°	.42	.58
1000°	.29	.71
1050°	.15	.85
1150°	.16	.84

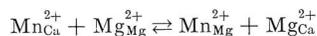
<sup>a</sup> (Estimated error  $\pm 0.05$ )

containing 0.005 percent Mn. It was obtained through the courtesy of Professors J. V. Smith and Paul B. Moore of the University of Chicago. Smith (1966) gave a microprobe analysis and quoted a chemical analysis by Ingamells for this sample. Since this diopside showed by far the narrowest EPR lines, a series of heating experiments were performed on this sample to determine the distribution of  $Mn^{2+}$  in the Ca- and Mg-sites as a function of temperature. The results of these experiments are given in Table 3 and Figures 4 and 5. The unheated sample contains about 76 percent  $Mn^{2+}$  in the Ca-site. The exchange begins at about 900°C and is essentially complete at 1050°C, at which point the  $Mn^{2+}$  distribution is reversed with 15 percent  $Mn^{2+}$  in the Ca-site.

The natural diopsides show a variety of  $Mn^{2+}$  distributions, which range from (a) most  $Mn^{2+}$  in the Ca-site, through (b) most  $Mn^{2+}$  in the Mg-site, to (c) all  $Mn^{2+}$  in the Mg-site. This range is illustrated by the  $Mn^{2+}$  EPR spectra of selected natural diopsides in Figure 6. The total Mn concentrations and the  $Mn^{2+}$  fractions in the Ca- and Mg-sites are given in Table 4. Results of spectrographic analysis of the diopsides are given in Table 5.

#### DISCUSSION

$Ca^{2+}$  is assumed to be localized only at the Ca-site of the diopside structure because of its large ionic size (0.99 Å), while  $Mn^{2+}$  and  $Mg^{2+}$  can be in both Ca- and Mg-sites. Since the ionic size of  $Mn^{2+}$  (0.80 Å) is much larger than that of  $Mg^{2+}$  (0.66 Å), for low Mn concentrations  $Mn^{2+}$  should prefer the Ca-site in diopside at low temperatures, provided  $Ca^{2+}$  deficiency at the Ca-site is available. This is the case in diopside, Y6. At higher temperatures an exchange between  $Mn^{2+}$  in the Ca-site and  $Mg^{2+}$  in the Mg-site is expected to occur; the exchange reaction can be written as:



the subscripts denoting Ca- and Mg-sites. This behavior would be similar to the  $Fe^{2+}$  distribution in orthopyroxenes,

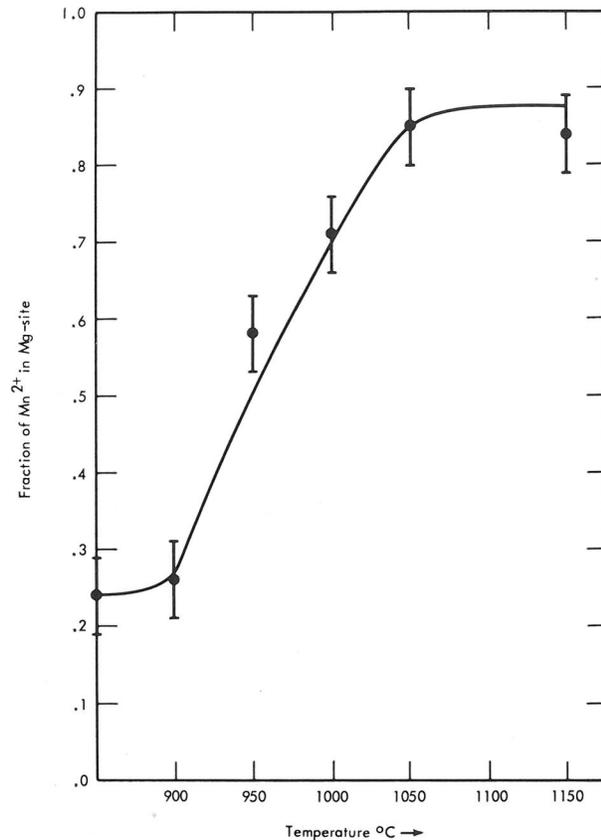
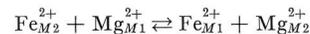


FIG. 5. Fraction of  $Mn^{2+}$  in the Mg-site of diopside, Y6, as a function of temperature.

where  $Fe^{2+}$  is preferred strongly at the M2 site, the pertinent exchange reaction being:



(Ghose, 1965; Ghose and Hafner, 1967). In the  $(Mn, Mg)_2Si_2O_6$  solid solution series,  $Mn^{2+}$ - $Mg^{2+}$  exchange is expected to be parallel to the  $Fe^{2+}$ - $Mg^{2+}$  exchange in

TABLE 4. DISTRIBUTION OF  $Mn^{2+}$  IN CA- AND MG-SITES AND TOTAL MN CONTENT OF SOME DIOPSIDES

Sample No.	Locality	Total Mn %	Fraction of $Mn^{2+}$ in	
			Ca-Site	Mg-Site
Y6	Twin Lakes, Cal.	0.005	0.76	0.24
78237	Siberia	.09	.55	.45
M14082	Tyringstown, Mass.	.1	.48	.52
U. of Chicago	Pitcairn, N. Y.	.02	.16	.84
11773	Natural Bridge, N. Y.	.03	.0	~1.0
73966	DeBeers Mine, S. Africa	~.001	.0	~1.0

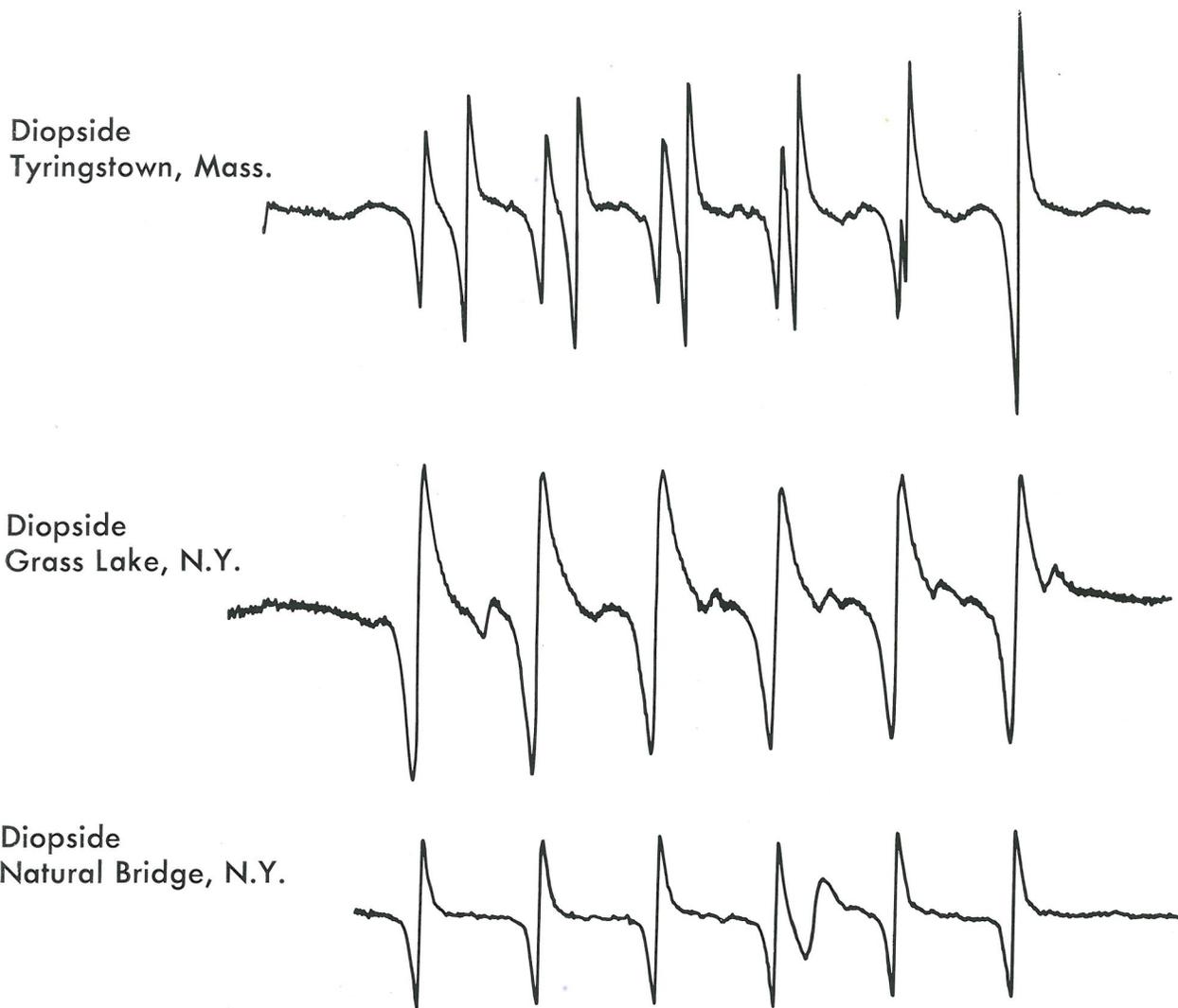
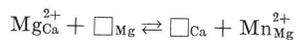


FIG. 6.  $Mn^{2+}$  EPR spectra ( $m = +\frac{1}{2} \rightarrow m = -\frac{1}{2}$ ) in some natural diopsides.

orthopyroxenes, with  $Mn^{2+}$  being preferred at the  $M2$  site. Since we are dealing with very low concentrations of Mn, an exchange involving lattice vacancies must also be considered. The exchange reaction between  $Mn^{2+}$  in the Ca-site and vacancies in the Mg-site can be written as:



where  $\square_{Ca}$  and  $\square_{Mg}$  denote vacancies at the Ca- and Mg-sites respectively. Until a complete kinetic study of the exchange reaction has been made, it is not possible to determine whether equilibrium has been established in our heating experiments, particularly at lower temperatures. Hence, the distribution curve in Figure 5 may not represent strictly an equilibrium situation.

TABLE 5. SPECTROGRAPHIC ANALYSIS OF DIOPSIDES

Sample No.	Locality	Al	Fe	Mn	Na	K	Ti
Y6	California	0.02	0.05	0.005	<0.01	<0.01	<0.003
78237	Siberia	.007	0.9	.09	<.01	<.01	.004
M14082	Tyringstown, Mass.	.2	1.0	.1	.04	.01	.008
U. of Chicago	Pitcairn, N.Y.	.3	.4	.02	.3	.08	.07
117733	Natural Bridge, N.Y.	.08	0.3	.03	.02	<.01	.003
All samples					Zn, Hg	<0.1	
	Li, Pb, Ba, Bi, Sr, Sb, Co, Cr, V, Mo, Sn, Zr					<0.01	
					Ni, Cu, Ag	<0.001	

Analyst: Doris Huff, Chemistry Division, Argonne National Laboratory.

For very low concentrations of Mn, most  $Mn^{2+}$  occurring in the Mg-site seems to be the equilibrium distribution at temperatures above 900°C. This idea is supported by similar  $Mn^{2+}$  distribution patterns found in two diopsides whose temperature of formation are known to be above 900°C. The first one is synthetic, made by D. A. Stephenson at the University of Chicago and contains very small amounts of Mn (not detected by microprobe: Smith, 1966). The second one is a chromediopside (USNM 75966) from Bullfontaine shaft, De Beers Mine, S. Africa obtained through the courtesy of Dr. Francis R. Boyd of the Geophysical Laboratory. It occurs in a kimberlite pipe and apparently crystallized around 1000°C. It contains ~ 0.001 percent Mn (Boyd, 1969 and priv. commun).

With higher concentration of Mn, the absolute concentration will have an effect on the  $Mn^{2+}$  distribution and above a certain threshold Mn concentration, more  $Mn^{2+}$  in the Mg site will be favored. However, there must be other factors involved as indicated by the distribution found in the diopside from Natural Bridge, N.Y. It shows all Mn in the Mg-site, yet the total Mn content is only 0.03 percent. This type of distribution could be caused by some other ion like  $Na^+$  completely blocking vacancies at the Ca-site, normally available to  $Mn^{2+}$ .

Apparently the effects of absolute concentration and other ions on the  $Mn^{2+}$  distribution must be understood before the observed distribution can be used as a temperature indicator with certainty. More  $Mn^{2+}$  in the Ca-site indicates a low temperature pattern. However, more  $Mn^{2+}$  in the Mg-site may or may not indicate a high temperature pattern. Further heating experiments on diopsides showing the low temperature pattern with different Mn concentrations as well as kinetic experiments on the  $Mn^{2+}$  exchange in diopside Y6 are in progress.

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