

ELECTRON PARAMAGNETIC RESONANCE OF  $Mn^{2+}$  IN DOLOMITE AND MAGNESITE, AND  $Mn^{2+}$  DISTRIBUTION IN DOLOMITESPETER SCHINDLER<sup>1</sup> *Chemistry Division, Argonne National Laboratory  
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## ABSTRACT

The spin Hamiltonian parameters of  $Mn^{2+}$  occurring in two different lattice sites in dolomite and in magnesite are:

	$g$	$D$ (Gauss)	$a$ (Gauss)	$A$ (Gauss)	$B$ (Gauss)
Dolomite					
Ca-site	2.0005 (15)	$\pm 3.2$ (2)	$\mp 7.1$ (3)	93.0 (3)	93.9 (3)
Mg-site	2.0005 (10)	151.9 (15)	10.25 (30)	93.0 (3)	91.8 (3)
Magnesite					
Mg-site	2.0010 (10)	$\pm 85.5$ (20)	$\mp 12.2$ (5)	92.1 (5)	93.0 (3)

The site assignment of the  $Mn^{2+}$  spectra in dolomite is based on the comparison of  $D$  parameters found in dolomite with those in calcite and magnesite respectively. Two types of  $Mn^{2+}$  distribution in natural dolomites have been found: (1) more  $Mn^{2+}$  in the Mg site, (2) all  $Mn^{2+}$  in the Mg site. Dolomite from Gabbs, Nev. shows the first type of distribution, while clear dolomite crystals from Binnental, Switzerland show the second type though both contain 0.08 Mn/100 cations.

## INTRODUCTION

Recently the distribution of trace amounts of  $Mn^{2+}$  in the Ca- and Mg-sites in diopside has been studied by electron paramagnetic resonance (EPR) (Ghose and Schindler, 1969). A similar situation exists in dolomite,  $CaMg(CO_3)_2$ , which also has two crystallographically distinct Ca- and Mg-sites. Dolomite crystallizes in the rhombohedral space group  $R\bar{3}$  with Ca at 1(a): 0, 0, 0 and Mg at 1(b):  $\frac{1}{2}$ ,  $\frac{1}{2}$ ,  $\frac{1}{2}$ . Both positions have point symmetry  $\bar{3}$ . Both Ca and Mg are surrounded by six oxygens in the form of an octahedron, each octahedral oxygen belonging to a different  $CO_3$  group. The Ca-O distance is 2.390 Å and the Mg-O distance 2.095 Å (Steinfink and Sans, 1959). The oxygen coordination octahedra around Ca and Mg are deformed along the threefold axis.

## THEORY

The spin Hamiltonian for the  $Mn^{2+}$  ion located in a crystalline electric

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field with trigonal symmetry (where the [111] axis of dolomite is the trigonal symmetry axis) is given by: (Bleany and Ingram, 1951; Vinokurov, Zaripov and Stepanov, 1961):

$$\begin{aligned} \mathfrak{H}C = & g\|\beta H_z S_z + g \perp \beta (H_x S_x + H_y S_y) + D[S_z^2 - \frac{1}{3}S(S+1)] \\ & + \frac{a}{6} [S_\xi^4 + S_\eta^4 + S_\zeta^4 - \frac{1}{3}S(S+1)(3S^2 + 3S - 1)] \\ & + \frac{F}{180} [35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2] \\ & + AS_z I_z + B(S_x I_x + S_y I_y) + Q[I_z^2 - \frac{1}{3}I(I+1)] - g_N \beta_N \mathbf{H} \cdot \mathbf{I}. \end{aligned}$$

The z-axis is parallel to the threefold axis, which coincides with the [111] axis in the crystalline coordinate system  $\xi, \eta, \zeta$ . Here,

$g$  = spectroscopic splitting factor

$g_N$  = nuclear  $g$ -factor

$\beta$  = Bohr magneton

$\beta_N$  = nuclear magneton

$\mathbf{H}_0$  = applied magnetic field

$D, F$  = axial components of the crystal field potential

$a$  = cubic component of the crystal field potential

$A, B$  = hyperfine splitting factors

$Q$  = nuclear quadrupole moment

#### EXPERIMENTAL

The rhombohedral cleavage fragments of carbonates were glued to a metal cylindrical jig, whereby the [111] axis of the crystal was parallel to the axis of the jig. Crystal sections were cut perpendicular to the [111] axis. The sections were glued to a lucite rod on a face ground normal to the [111] axis, so that this axis could be rotated in a horizontal plane containing  $H_0$ .

All measurements were made on a Varian V-4500 EPR spectrometer at 9.5 GHz. The fieldial control of the magnetic field was calibrated against a NMR probe and the line positions were measured with the Fieldial. The frequency was measured with the wave meter supplied with the microwave bridge. All EPR measurements were made at room temperature. The crystals were mounted on a lucite rod in a cylindrical  $TE_{011}$  cavity.

To determine relative  $Mn^{2+}$  concentration at each site, the second moments of the first derivative of the absorption lines were computed. The lines recorded, when the [111] axis is normal to  $H_0$ , showed maximum resolution of the principal lines ( $M = +\frac{1}{2} \leftrightarrow -\frac{1}{2}$ ) and hence were used for such measurements (Fig. 1a and b). Usually the two sets showed different saturation behavior, so care had to be taken to prevent saturation of either set.

#### RESULTS

Spin Hamiltonian parameters for  $Mn^{2+}$  in the Mg-site were measured in a dolomite crystal from Binnental, which showed practically no

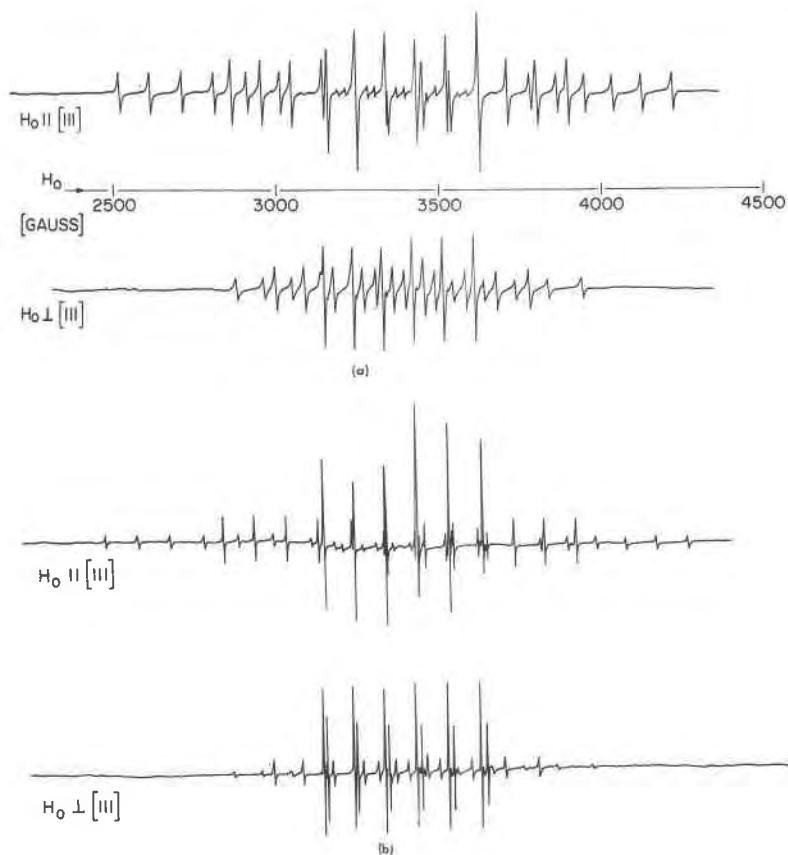


FIG. 1. EPR spectra of  $Mn^{2+}$  in dolomite from (a) Binnental, Switzerland, and (b) Oberdorf, Styria, Austria, with the [111] axis parallel and perpendicular to the direction of the applied magnetic field,  $H_0$ .

$Mn^{2+}$  in the Ca-site, and hence there was no interference from  $Mn^{2+}$  resonance lines in the Ca-site (Figs. 1a). A dolomite crystal from Oberdorf, Styria, Austria showing  $Mn^{2+}$  in both sites was used for the measurement of the spin Hamiltonian parameters of  $Mn^{2+}$  in the Ca-site (Fig. 1b) (Schindler and Ghose, 1969). Because of the narrow line widths found in this crystal, it was possible to separate the crystal field parameter ' $D$ ' from ' $a$ ' and ' $F$ '. The results are listed in Table 1 along with those by Vinokurov, Zaripov and Stepanov (1961). Note that Vinokurov, *et al.* (1961) did not succeed in separating ' $D$ ' from ' $a-F$ ', largely due to the larger line widths encountered in the crystal they used for their investigation. The spin Hamiltonian parameters for  $Mn^{2+}$  measured in a

TABLE 1. SPIN HAMILTONIAN PARAMETERS OF  $Mn^{2+}$  IN SOME CARBONATES  
All Values are in Gauss Except  $g$ .

Mineral	$g$	$D$	$a, F$	$A$	$B$	Reference
Calcite $CaCO_3$	$\parallel 2.0022 \pm 6$	$\parallel 40.5 \pm 2$				
	$\perp 2.0014 \pm 6$	$\perp 39.7 \pm 2$	$a = 0.0428 \pm 20$	$93.95 \pm 5$	$93.90 \pm 5$	Hurd <i>et al.</i> (1954)
	$2.0009 \pm 1$	$27.69 \pm 1$	$a = 0.043 \pm 1$	$94.94 \pm 1$	$94.94 \pm 1$	Serway (1967)
Smithsonite $ZnCO_3$	$2.003 \pm 1$	$\mp 44.33 \pm 1$	$a - F = \pm 12.2 \pm 1$	$\mp 92.0 \pm 1$	$\pm 92.8 \pm 1$	Burley (1964)
	$2.0008 \pm 2$	$(-)\ 1.4 \pm 3$	$F = (+)\ 8.75 \pm 25$	$(+)\ 93.50 \pm 25$	$(+)\ 93.75 \pm 25$	Grechusnikov & Koryagin (1966)
Magnesite $MgCO_3$	$2.0010 \pm 10$	$\pm 85.5 \pm 20$	$a = \pm 12.2 \pm 5$	$92.1 \pm 2$	$93.0 \pm 2$	This paper
	$2.001$	$\pm 85.5$	$a - F = \pm 12.1$	$\pm 92.0$	$\pm 93.0$	Vinokurov <i>et al.</i> (1961)
Dolomite $CaMg(CO_3)_2$ Ca-site	$2.0005 \pm 15$	$\pm 3.2 \pm 2$	$a \mp 7.1 \pm 3$	$93.0 \pm 3$	$93.9 \pm 3$	This paper
	$2.003$		$2D - \frac{2}{3}(a - F) = \pm 11$	$\pm 93.4$		Vinokurov <i>et al.</i> (1961)
Mg-site	$2.0005 \pm 10$	$151.9 \pm 1.5$	$a = 10.25 \pm 3$	$93.0 \pm 0.3$	$91.8 \pm 3$	This paper
	$2.003$	$\pm 153.2$	$a - F = \pm 10.4$	$\pm 93.4$	$\pm 94.3$	Vinokurov <i>et al.</i> (1961)
Ankerite $Ca(Mg, Fe)(CO_3)_2$	$2.003$	$\approx 150$	?	92	?	Vinokurov <i>et al.</i> (1961)
	$2.003$	$\approx 140$	?	94	?	Vinokurov <i>et al.</i> (1961)

TABLE 2. DISTRIBUTION OF  $Mn^{2+}$  IN Ca- and Mg-SITES IN SOME DOLOMITE CRYSTALS

Sample No.	Locality	Total Mn	Fraction of $Mn^{2+}$ in	
			Ca-site	Mg-site
SG 677	Binnental, Switzerland	0.08/100 cations	0.3	0.97
J.R.G.	Gabbs, Nevada	0.08/100 cations	0.376	0.624
USNM, R12596	Oberdorf, Styria, Austria	n.d.	0.375	0.627

magnesite crystal from Trieben, Styria, Austria are listed in Table 1 along with the parameters determined by Vinokurov *et al.* (1961). The  $Mn^{2+}$  fractions at the Ca- and Mg-sites in dolomites from Binnental, Switzerland; Gabbs, Nevada, and Oberdorf, Styria, Austria are listed in Table 2.

#### DISCUSSION

*Site Assignment.* Vinokurov *et al.* (1961) have assigned the  $Mn^{2+}$  spectra with a larger '*D*' to the Mg site, principally on the basis of mineral chemical evidence. This site is most populated by  $Mn^{2+}$  as seen from the EPR spectra and the chemical analysis of all dolomites with considerable  $Mn^{2+}$  indicate that practically all of the  $Mn^{2+}$  must occur in the Mg-site (Goldsmith, 1959). In a study of the  $CaCO_3$ - $MgCO_3$ - $MnCO_3$  system, Goldsmith and Graf (1960) found that  $Mn^{2+}$  substitutes for  $Mg^{2+}$  more readily than  $Ca^{2+}$  in dolomite. However, the crystal-chemical behavior of  $Mn^{2+}$  as a major element may not necessarily be the same as when  $Mn^{2+}$  occurs in trace mounts. In an EPR study of natural dolomite powders, Wildeman (1970) has made the same site assignment as Vinokurov *et al.* (1961) based on the hyperfine splitting parameter '*A*'. The '*A*' parameters for  $Mn^{2+}$  in MgO and  $MgCO_3$  are slightly smaller than they are in CaO and  $CaCO_3$  respectively. On this basis he assumed that the site showing the smaller '*A*' parameter for  $Mn^{2+}$  (but with larger '*D*') must be the Mg-site.

We have independently arrived at the same site assignment through another path, namely by comparing the crystal field parameters '*D*' of  $Mn^{2+}$  in calcite,  $CaCO_3$ , magnesite,  $MgCO_3$  and the two sites in dolomite  $CaMg(CO_3)_2$  (Table 1). The underlying assumption is that the structures of the octahedral Ca-O and Mg-O layers in dolomite must be closely similar to those in calcite and magnesite respectively. Note that the crystal field parameter '*D*' for  $Mn^{2+}$  in calcite (27.69G) is much smaller than that in magnesite (85.5G). Accordingly, we assign the spectra with a smaller '*D*' (3.2G) to the Ca-site in dolomite and with the larger '*D*' (151.9G) to the Mg-site in dolomite. It is gratifying to note that all three approaches lead to the same site assignment.

*Crystal Field Parameters.* The crystal field parameter ' $D$ ' for  $Mn^{2+}$  in the Ca-site in dolomite is very small (3.2G) while that at the Mg-site is the largest (151.9G) measured so far in a carbonate (Table 1). Usually ' $D$ ' is taken as a measure of the axial distortion of the crystal field from cubic symmetry. The cation-oxygen octahedron in a rhombohedral carbonate can be distorted only by stretching or compressing along the octahedral axis, which coincides with the  $\bar{3}$  axis running parallel to [111] axis in the crystal. On the basis of the increasing ' $D$ ' parameter, the carbonates can be arranged in the following order (see Table 1):

Otavite	<	Dolomite	<	Calcite	<	Smithsonite	<	Magnesite	<	Dolomite
$CdCO_3$		$CaMg(CO_3)_2$		$CaCO_3$		$ZnCO_3$		$MgCO_3$		$CaMg(CO_3)_2$
		Ca-site								Mg-site

Hence, the degree of axial distortion of the cation-oxygen octahedron must increase in the same order. It would be interesting to confirm this prediction from accurate crystal structure refinements of these carbonates.

*Mn<sup>2+</sup> Fractionation Between the Ca- and the Mg-site in Dolomite.* For very small concentration of  $Mn^{2+}$  (~100 ppm) in a dolomite showing narrow lines (~2-3 Gauss), the fractionation of  $Mn^{2+}$  between the Ca-site and the Mg-site can be determined quite accurately. However, with increasing  $Mn^{2+}$  content the lines broaden and the two sets of lines overlap, thereby drastically reducing the accuracy of the determination. After examining a number of dolomite crystals with known or unknown Mn content, we found dolomite crystals from three localities, namely Binnental, Switzerland; Gabbs, Nevada and Oberdorf, Styria, Austria yield narrow enough lines for such determination with any accuracy. Though the accuracy is difficult to determine, it is believed to be  $\pm 10$  percent of the amount present. These fractionation studies show two types of  $Mn^{2+}$  distribution: (1) practically all the  $Mn^{2+}$  in the Mg site (e.g. dolomite from Binnental), and (2) most  $Mn^{2+}$  in the Mg-site (e.g. dolomite from Styria, Austria). Unlike the case of diopsides no dolomite has been found yet showing most  $Mn^{2+}$  in the Ca-site.

The dolomite single crystal from an unstated locality investigated by Vinokurov *et al.* (1961), as well as dolomite powders from the Leadville Formation, Gilman, Colorado and Byron Formation, Door County, Wisconsin, investigated by Wildeman (1970) show the second type of distribution, namely most  $Mn^{2+}$  in the Mg-site. Furthermore, Wildeman (1970) found an interesting correlation among the total  $Mn^{2+}$  content, the fractionation of  $Mn^{2+}$  between two sites and the location of the dolomite bed of the Leadville Formation with reference to the ore body. The total

Mn content, as well as, the fraction of  $Mn^{2+}$  in the Mg-site increase as one approaches the ore body. Wildeman (1970) could not decide whether this effect is due to fluid contact or heat.

From  $Mn^{2+}$  EPR studies on a diopside from California (Ghose and Schindler, 1969) initially showing more  $Mn^{2+}$  in the Ca-site, it was found that heat treatment above  $950^{\circ}C$  leads  $Mn^{2+}$  to migrate from the Ca-site to the Mg-site. In dolomite, we can visualize a similar  $Mn^{2+}$  migration from the Ca-site to the Mg-site as a function of temperature, which can explain the observations of Wildeman (1970). To test this hypothesis, millimeter size dolomite cleavage fragments from Gabbs, Nevada were heated at 1 kbar  $CO_2$  pressure up to a temperature of  $700^{\circ}C$  in a cold seal pressure vessel for a period of 1 week. The EPR spectra of the samples recorded before and after heating indicated no  $Mn^{2+}$  exchange. This probably means that in dolomite the threshold temperature at which the  $Mn^{2+}$  migration begins is higher than  $700^{\circ}C$ .

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#### REFERENCES

- BLEANY, B., AND D. J. E. INGRAM (1951) The paramagnetic resonance spectra of two salts of manganese. *Proc. Roy. Soc. (London) A*, **205**, 336-356.
- BURLEY, S. P. (1964) The allowed and forbidden transitions in the paramagnetic resonance of the manganese ion in trigonal sites in apatite and smithsonite. *Aust. J. Phys.* **17**, 537-42.
- GHOSE, S., AND P. SCHINDLER (1969) Determination of the distribution of trace amounts of  $Mn^{2+}$  in diopsides by electron paramagnetic resonance. *Mineral. Soc. Amer. Spec. Pap.* **2**, 51-58.
- GOLDSMITH, J. R. (1959) Some aspects of the geochemistry of carbonates. in: P. H. Abelson (editor), *Researches in Geochemistry*, John Wiley, New York, **1**, 336-358.
- , AND D. L. GRAF (1960) Subsolidus relations in the system  $CaCO_3$ - $MgCO_3$ - $MnCO_3$ . *J. Geol.* **68**, 324-335.
- GRECHUSNIKOV, V. N., AND V. F. KORYAGIN (1966) Paramagnetic resonance of the  $Mn^{2+}$  ion in synthetic otavite,  $CdCO_3$ . *Fiz. Tverd. Tela* **7**, 3123-3126 [Transl. *Sov. Phys. Solid State*, **7**, 2527-2528].
- HURD, F. K., M. SACHS, AND W. D. HERSHBERGER (1954) Paramagnetic resonance absorption of  $Mn^{2+}$  in single crystals of  $CaCO_3$ . *Phys. Rev.* **93**, 373-380.
- SCHINDLER, P., AND S. GHOSE (1969) Electron paramagnetic resonance of  $Mn^{2+}$  in dolomite  $CaMg(CO_3)_2$ , and magnesite,  $MgCO_3$ , and the  $Mn^{2+}$  distribution in dolomites. [abstr.], *Trans. Amer. Geophys. Union*, **50**, 357.
- SERWAY, R. A. (1967) *Paramagnetic Defect Centers in Single Crystal Calcite*. Ph.D. Thesis, Illinois Institute of Technology, Chicago, Ill.

- STEINFINK, H. AND F. J. SANS (1959) Refinement of the crystal structure of dolomite. *Amer. Mineral.* **44**, 679-682.
- VINOKUROV, V. M., M. M. ZARIPOV, AND V. G. STEPANOV (1961) A study of some Mn containing carbonates by the method of electron paramagnetic resonance. *Kristallografiya* **6**, 104-108 [Transl. *Sov. Phys. Crystallogr.*, **6**, 83-86].
- WILDEMAN, T. R. (1970) The distribution of  $Mn^{2+}$  in some carbonates by electron paramagnetic resonance, *Chem. Geol.* **5**, 167-177.

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