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ELECTRON PARAMAGNETIC RESONANCE OF Mn^{2+} IN DOLOMITE AND MAGNESITE, AND Mn^{2+} DISTRIBUTION IN DOLOMITES

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ABSTRACT

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

Dolomite	g	D (Gauss)	a (Gauss)	A (Gauss)	B (Gauss)
Ca-site	2.0005 (15)	±3.2 (2)	∓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)	±85.5 (20)	∓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):

$$\begin{aligned}\mathcal{H} = {} & g_{\|}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + D[S_z^2 - \tfrac{1}{3}S(S+1)] \\ & + \frac{a}{6}[S_\xi^4 + S_\eta^4 + S_\zeta^4 - \tfrac{1}{5}S(S+1)(3S^2+3S-1)] \\ & + \frac{F}{180}[35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2] \\ & + AS_zI_z + B(S_xI_x + S_yI_y) + Q[I_z^2 - \tfrac{1}{3}I(I+1)] - g_N\beta_N \boldsymbol{H}\cdot\boldsymbol{I}.\end{aligned}$$

The z-axis is parallel to the threefold axis, which coincides with the [111] axis in the crystalline coordinate system ξ, η, ζ. Here,

g = spectroscopic splitting factor
g_N = nuclear g-factor
β = Bohr magneton
β_N = nuclear magneton
$\boldsymbol{H}_0$ = 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

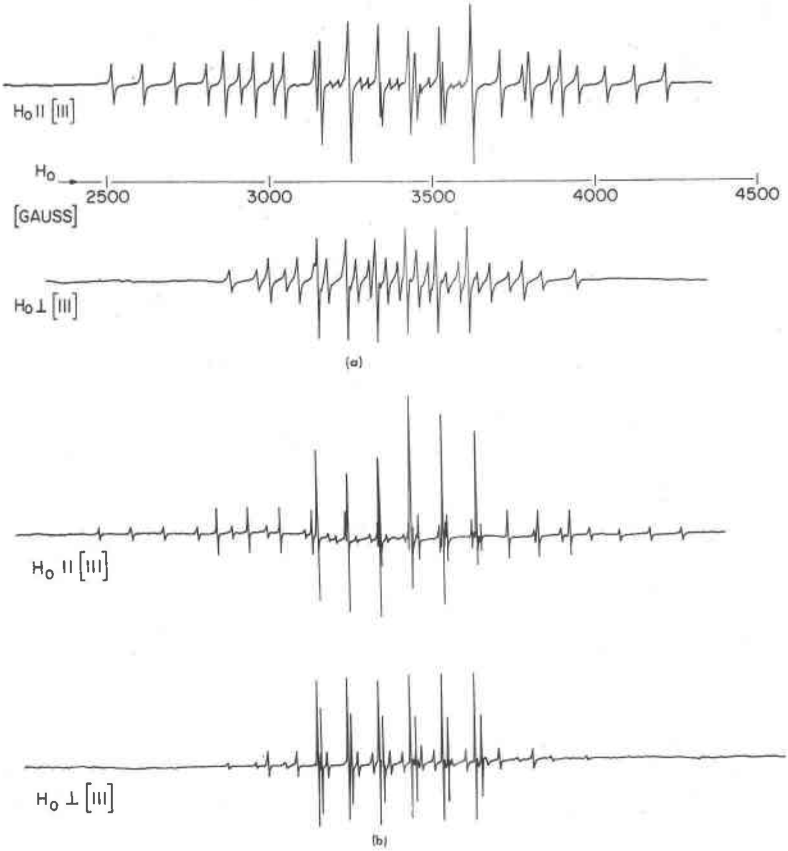

FIG. 1. EPR spectra of Mn^{2+} in dolomite from (a) Binnental, Switzerland, and (b) Oberdorf, Styria, Austria, with the [111] axis parallel and perpendicular to the direction of the applied magnetic field, H_0.

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	$\parallel 2.0022\pm6$	$\parallel 40.5\pm2$				
$CaCO_3$	$\perp 2.0014\pm6$	$\perp 39.7\pm2$	$a=0.0428\pm20$	93.95 ± 5	93.90 ± 5	Hurd *et al.* (1954)
	2.0009 ± 1	27.69 ± 1	$a=0.043\pm1$	94.94 ± 1	94.94 ± 1	Serway (1967)
Smithsonite						
$ZnCO_3$	2.003 ± 1	$\mp44.33\pm1$	$a-F=\pm12.2\pm1$	$\mp92.0\pm1$	$\pm92.8\pm1$	Burley (1964)
Otavite						
$CdCO_3$	2.0008 ± 2	$(-)1.4\pm3$	$F=(+)8.75\pm25$	$(+)93.50\pm25$	$(+)93.75\pm25$	Grechusnikov & Koryagin (1966)
Magnesite						
$MgCO_3$	2.0010 ± 10	$\pm85.5\pm20$	$a=\pm12.2\pm5$	92.1 ± 2	93.0 ± 2	This paper
	2.001	±85.5	$a-F=\pm12.1$	±92.0	±93.0	Vinokurov *et al.* (1961)
Dolomite						
$CaMg(CO_3)_2$						
Ca-site	2.0005 ± 15	$\pm3.2\pm2$	$a\mp7.1\pm3$	93.0 ± 3	93.9 ± 3	This paper
	2.003		$2D-\frac{2}{3}(a-F)=\pm11$	±93.4		Vinokurov *et al.* (1961)
Mg-site	2.0005 ± 10	151.9 ± 1.5	$a=10.25\pm3$	93.0 ± 0.3	91.8 ± 3	This paper
	2.003	±153.2	$a-F=\pm10.4$	±93.4	±94.3	Vinokurov *et al.* (1961)
Ankerite						
$Ca(Mg,\ Fe)(CO_3)_2$	2.003	≈150	?	92	?	Vinokurov *et al.* (1961)
Breunerite						
$(Mg,\ Fe)\ CO_3$	2.003	≈140	?	94	?	Vinokurov *et. al.* (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^{2+} Fractionation Between the Ca- and the Mg-site in Dolomite. For very small concentration of Mn^{2+}($\sim$100 ppm) in a dolomite showing narrow lines ($\sim$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 ±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 fractiontion 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°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°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°C.

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