

ELECTRON SPIN RESONANCE OF Mn^{2+} IMPURITIES IN NEWBERYITE

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ABSTRACT

The electron spin resonance of Mn^{2+} impurities in natural crystals of newberyite, $8(MgHPO_4 \cdot 3H_2O)$, was studied in the 9.2 GHz microwave frequency range and at room temperature. Two differently oriented, but otherwise equivalent, magnetic complexes of Mn^{2+} were found. The complexes were related to each other by two-fold symmetry about the crystallographic b axis. The resonance lines were fitted to a spin Hamiltonian of rhombic symmetry and the following parameters were determined:

$g = 1.9995(5)$, $b_2^0 = 253.5(1.5)$, $b_2^2 = 252.0(1.5)$, $b_4^0 = -0.79(.10)$, $A = 89.7(1.5)$, $B = 88.2(1.5)$.

The values of b_n^m , A , and B are in units of 10^4 cm⁻¹. The results are compared to those obtained in struvite, which is a mineral that can decompose into newberyite.

INTRODUCTION

The electron spin resonance (ESR) technique is used to study Mn^{2+} paramagnetic impurity ions in natural crystals of newberyite, $8(MgHPO_4 \cdot 3H_2O)$. The study affords an opportunity to study manganese impurities coordinated by mixed types of ligands, these being three water molecules and three oxygen ions for the two inequivalent Mg^{2+} cation sites in newberyite. It also allows one to make comparisons between the magnetic behavior of newberyite and struvite, $2(MgNH_4PO_4 \cdot 6H_2O)$, since the ESR of Mn^{2+} in struvite has been reported previously by Vinokurov and Tukhvatullin (1968). This is of interest because struvite is known to decompose into newberyite. Newberyite appears to be an altered lower hydration derivative of struvite. There is also a possibility that struvite and newberyite can form independently from the same organic matter, but no definite proof of this has been found.

The newberyite crystals used in this work originated from the Skipton caves, Victoria, Australia, where they are known to form from bat guano. The crystals were of fairly good quality with well-defined faces, and had dimensions of approximately $7 \times 6 \times 5$ mm. The X-ray crystallography of newberyite has been reported by Sutor (1967). The crystal is orthorhombic with space group $Pbca$, and lattice parameters $a = 10.215$, $b = 10.681$, and $c = 10.014$ Å. The

projection of the unit cell on the (010) plane is shown in Figure 1. The two inequivalent magnesium sites, labeled MgI and MgII in the figure, are identical to each other, but they are differently oriented in the unit cell. The ESR results give information about the distortion of the sites, the orientation of the magnetic complexes, and the amount of covalent bonding in the manganese coordinated sites.

The X-ray crystallography of struvite has been reported by Whitaker and Jeffery (1970a and 1970b). The crystal is orthorhombic with space group $Pmn2_1$ and cell dimensions $a = 6.941$, $b = 6.137$, and $c = 11.199$ Å. There are two non-equivalent magnesium sites in struvite, and each site is coordinated by a near octahedron of six water molecules.

In this study we have determined the pertinent spin Hamiltonian parameters of Mn^{2+} in newberyite and have compared the results with manganese in struvite. In particular, we have attempted to correlate the covalency of a system consisting of manganese coordinated with three water molecules and three oxygen ions in terms of systems which are coordinated exclusively by waters or oxygens. The correlation is done in terms of Pauling's (1960) covalency parameter.

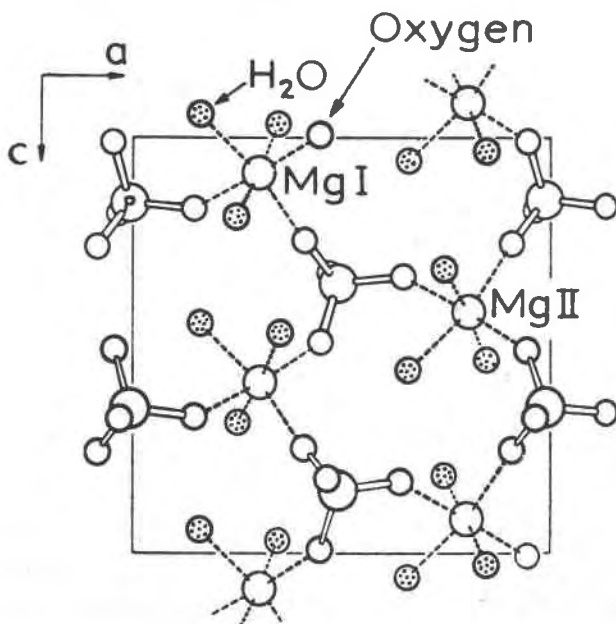


FIG. 1. Projection of unit cell of newberyite on (010), showing the magnesium coordination.

This parameter is based on the electronegativity property, which is the power of an atom in a molecule to attract electrons to itself.

EQUIPMENT AND EXPERIMENTAL PROCEDURE

The ESR measurements were done at X-band microwave frequencies (9.2 GHz), and at room temperature. The spectrometer, employing an 8 in. Newport magnet, was manufactured by Hilger and Watts Company. The microwave frequency was stabilized to an auxiliary cavity by means of a pound stabilizer system. The operating frequency was read off the same calibrated cavity. A phase-sensitive detection system was used and the signals were recorded on a strip chart recorder. The magnetic field was modulated at 100 kHz.

The crystal was glued to a perspex pin and mounted in a rectangular TE₁₀₂ cavity in such a way that it could be rotated about a horizontal axis. The magnet was rotated about a vertical axis and so it was possible to align the magnetic field direction along the magnetic complex axes of the crystal. The results were plotted on a stereographic projection net. The magnetic field positions of the ESR lines were measured by employing proton resonance. By placing the crystal with attached pin on a standard X-ray goniometer, it is possible to correlate the magnetic axes with the crystallographic axes, as determined by X-ray measurements. The correlation can be done in a simple and unambiguous way if the coordinate angles of the stereogram are correctly labeled. The labeling is determined by the way the crystal is aligned in the cavity and on the X-ray goniometer, by virtue of alignment markings on the crystal pin. The process has been described by Manoogian (1971).

RESULTS

Two identical, but differently oriented, magnetic complexes of Mn²⁺ were found in newberyite. The magnetic complexes exhibit rhombic symmetry, with the two *z* axes making an angle of 120° to each other. The complexes are related by twofold symmetry with respect to the crystallographic *b* axis, but none of the magnetic axes are constrained along the *b* direction. The relationship between the magnetic and crystallographic axes in newberyite is given in the stereogram of Figure 2. The angles between the axes, as obtained from the stereogram, are given in Table 1.

Two identical, but differently oriented, manganese complexes were also found in struvite by Vinokurov and Tuhvatullin (1968). Each of the complexes in this case have a common magnetic axis constrained along the crystallographic *a* axis, and the remaining magnetic axes are in the (100) plane. This is because the [100] direction is equivalent for the two Mg·6H₂O complexes in struvite.

The magnetic axes are defined when the five groups of six hyperfine lines of manganese in a given complex show extrema in their separations as a function of the magnetic field strength. This occurs when the external magnetic field is directed along the three perpendicular axes

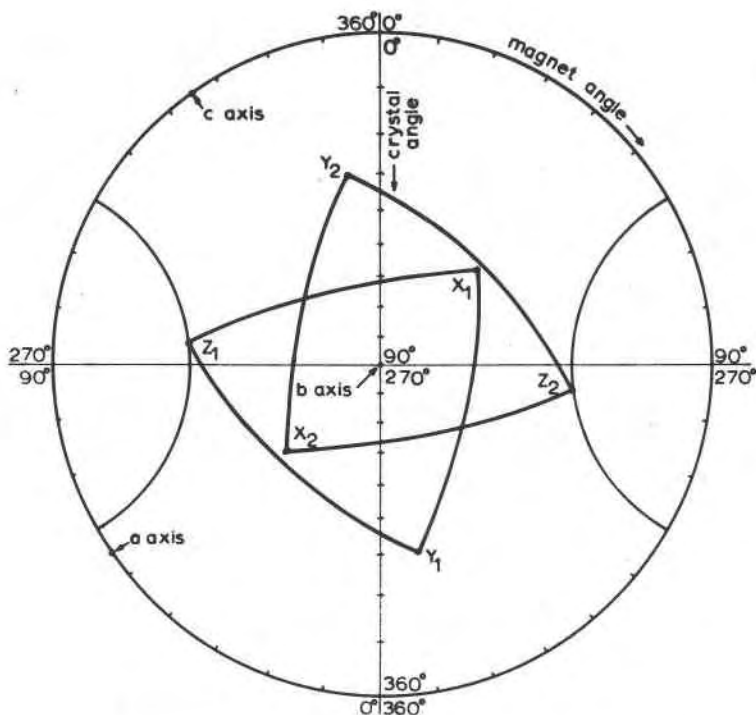


FIG. 2. Stereogram showing the relationship between the Mn^{2+} magnetic axes and the crystallographic axes in newberyite.

of the crystal field tensor. The z axis is defined as the direction of greatest separation of the hyperfine groups of lines. The y axis is 90° to the z axis and the groups of lines have a smaller separation in this direction. The x axis is mutually perpendicular to the z and y axis, and the groups show an even smaller separation in this direction. A typical chart recording of the ESR spectral lines in newberyite when the magnetic field direction is along one of the z axes is given in Figure 3. As seen in this figure, the linewidths are fairly broad and some of the spectral lines overlap with each other. Near the center of the spectrum the central group of hyperfine lines is also mixed with the lines of the second manganese complex. Hence there is some difficulty in obtaining accurate magnetic field positions of the ESR lines.

Magnetic field measurements were made along the z and y magnetic axes. No measurements could be made along the x axes since the lines are all mixed together and the various transitions cannot be distin-

TABLE I

Angular relationships between the magnetic and crystallographic axes of Mn^{2+} in newberyite (accuracy $\pm 2^\circ$).

Axes	a	b	c	X_2	Y_2	Z_2
a				48°	110°	130°
b				43°	62°	60°
c				95°	35°	125°
X_1	132°	43°	85°	86°		
Y_1	70°	62°	145°		124°	
Z_1	50°	60°	55°			120°

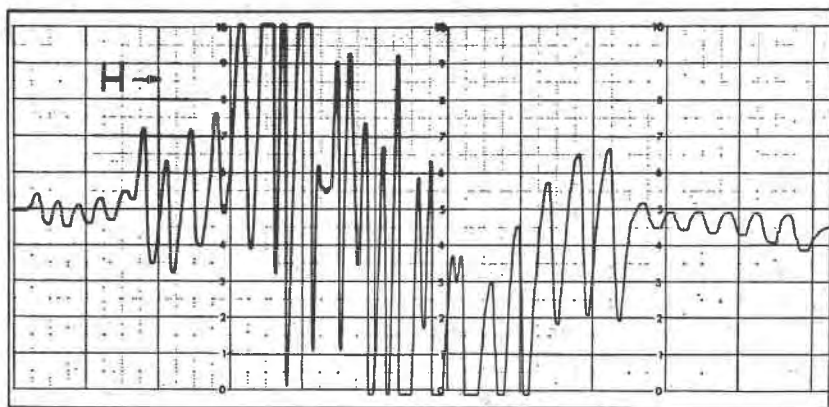


FIG. 3. Typical chart recording of Mn^{2+} in newberyite when the magnetic field direction is along a z axis.

guished. The results were fitted to a spin Hamiltonian of the form

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

where the terms have their usual meanings. Expressions for the positions of the ESR lines as a function of the magnetic field strength has been given to the second order of perturbation theory by Vinokurov *et al.* (1964). The values of the spin Hamiltonian parameters for the two identical manganese complexes are given in Table 2. The parameters b_4^2 and b_4^4 could not be found with any degree of precision for measurements along the magnetic axes because they have only a small effect when employing second-order perturbation theory.

No measurements were made for struvite since the work has been done by Vinokurov and Tukhvatullin (1968). However, for comparison purposes we have recorded in Figure 4 a spectral diagram obtained when the magnetic field was directed along the z axis of one of the manganese complexes. A good quality struvite crystal was available to obtain the diagram. As seen in this figure, the ESR lines have narrower linewidths and there is a greater separation between groups of hyperfine lines than in the case of newberyite. The spin Hamiltonian parameters reported for struvite are also listed in Table 2.

DISCUSSION AND CONCLUSIONS

The two manganese complexes in newberyite can be related to the two types of magnesium sites labeled MgI and MgII in Figure 1. These two sites are identical to each other but they are differently oriented in the unit cell. The angular relationships between the magnetic axes, as listed in Table 1, give a measure of the rotation of the two sites.

The spin Hamiltonian parameters b_2^0 and b_2^2 indicate that the magnesium sites exhibit a strong rhombic distortion. Furthermore, the distortion of the sites is such that the value of the rhombic parameter b_2^2 is almost identical to the value of the axial parameter b_2^0 . In struvite the value of b_2^2 was found to be much smaller than the value of b_2^0 , indicating less rhombic distortion in the $\text{Mg} \cdot 6\text{H}_2\text{O}$ sites compared with the $\text{Mg} \cdot (3\text{H}_2\text{O} + 3\text{O}^{2-})$ sites of newberyite.

TABLE II

Some spin Hamiltonian parameters of Mn^{2+} in newberyite and in struvite

Parameter	Newberyite	Struvite ^a
g	1.9995(5)	2.0004
b_2^0	$253.5(1.5) \times 10^{-4} \text{ cm}^{-1}$	$289.0 \times 10^{-4} \text{ cm}^{-1}$
b_2^2	252.0(1.5) "	87.6 "
b_4^0	- .79(10) "	2.9 "
A	89.7(1.5) "	88.3 "
B	88.2(1.5) "	88.5 "
C	-	87.5 "

^a Vinokurov and Tukhvatullin (1968).

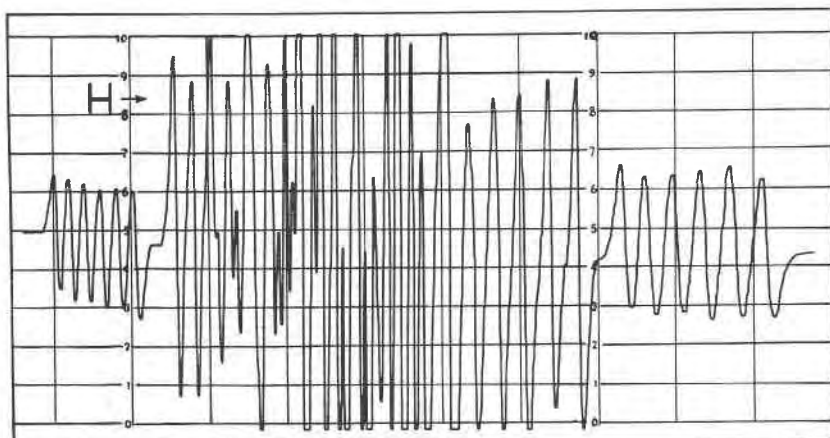


FIG. 4. Typical chart recording of Mn^{2+} in struvite when the magnetic field direction is along a z axis.

This is a result of particular interest to us since we have previously studied an analogous situation for the case of Cr^{3+} impurities in soda alum, $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, and in a crystal labeled "pseudo soda alum" (Manoogian and Danilov (1970)). Both of these crystals were formed when a saturated solution of sodium sulfate and aluminum sulfate slowly evaporated. In the case of soda alum the $\text{Cr}^{3+} \cdot 6\text{H}_2\text{O}$ sites exhibit axial symmetry, with the value of b_2^2 being zero. The sites in "pseudo soda alum", however, exhibit a strong rhombic distortion with the value of b_2^2 being nearly identical to the value of b_2^0 . The crystallography of a "pseudo soda alum" has never been done, but it is believed that this crystal is a lower hydration form of soda alum. Possibly some of the coordinated ligands in the aluminum sites of "pseudo soda alum" are oxygen ions. The angle between the two z magnetic axes of manganese in newberyite was found to be 120° , while the angle between the two z magnetic axes of Cr^{3+} in "pseudo soda alum" was 60° .

The magnitude of the hyperfine parameter A gives a measure of the amount of covalent bonding in the manganese complexes. The greater the covalent bonding, the smaller will be the hyperfine splitting.

The nature of the covalency parameter c has been described by Simanek and Muller (1970); and a plot of the hyperfine parameter A of Mn^{2+} versus the covalency has been produced by them for simple crystal systems. The monotonic part of their curve has been reproduced in Figure 5. The abscissa in this figure is the covalency parameter c divided by the number of ligands n , written as a percentage. This gives the average covalency per bond for the complex molecule, which is the Mn^{2+} ion plus the coordinated ligands. The ordinate of the curve in Figure 5 has been labeled $(|A| + |B|)/2$ for our purposes, since the average value of the hyperfine splitting parameter should give a better representation of the amount of covalent bonding present in the complicated crystals.

In a previous study (Kiggins and Manoogian, 1971), we have computed values of $(|A| + |B|)/2$ for a number of complicated crystals which have Mn^{2+} ions coordinated by $6 \cdot \text{H}_2\text{O}$ or by $6 \cdot \text{O}^{2-}$. The compiled results for the particular types of ligands were then averaged to give typical values of $(|A| + |B|)/2$. From the curve of Figure 5 it was then possible to obtain corresponding values for the covalency. The value for a typical $\text{Mn}^{2+} \cdot 6\text{H}_2\text{O}$ complex was determined as $c/n = 7.0$ percent, and for $\text{Mn}^{2+} \cdot 6\text{O}^{2-}$ as $c/n = 11.2$ percent. These average values of covalency are thought to be significant, and deviations from them could indicate a more complicated bonding involving other atoms in the crystal unit cell.

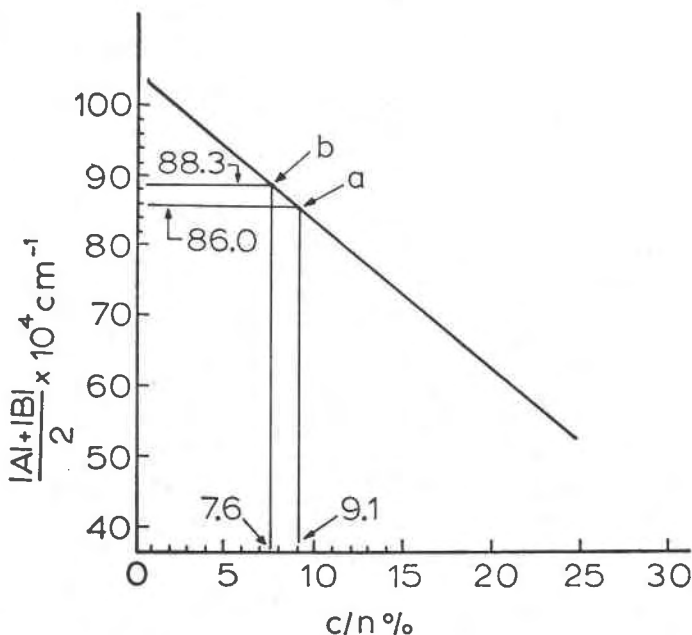


Fig. 5. Monotonic plot of the average hyperfine interaction parameter of Mn^{2+} versus the covalency parameter c divided by the number of ligands n . (Taken from Simanek and Muller, 1970). *a* indicates newberyite, *b* indicates struvite.

We can use the determined average values of covalency to predict what the values should be in systems where manganese is coordinated by mixed ligands of waters and oxygens. For the case of newberyite, where the coordination is by three waters and three oxygens, we have $c/n = (3 \times 7.0 + 3 \times 11.2)/6 = 9.1$ percent. From the curve of Figure 5 this gives a predicted $(|A| + |B|)/2$ value of $86.0 \times 10^{-4} \text{ cm}^{-1}$. The experimental value was found to be $89.0(1.5) \times 10^{-4} \text{ cm}^{-1}$, and so there is a slight discrepancy between the two values. The discrepancy could indicate a more complicated bonding involving other atoms in the unit cell. In a previous ESR experiment involving Mn^{2+} in blodite (Kiggins and Manoogian, 1971), where the coordinated ligands are four waters and two oxygens, this type of calculation gave better agreement between experimental and predicted values of $(|A| + |B|)/2$.

The average value of the hyperfine parameter for Mn^{2+} in struvite is $88.3(5) \times 10^{-4} \text{ cm}^{-1}$. This corresponds to a c/n value of 7.6 percent, which differs somewhat from the predicted value of 7.0 percent for a

$Mg^{2+} \cdot 6H_2O$ complex. This discrepancy also indicates a bonding more complicated than the ideal case. In fact, a more complicated bonding has been predicted for struvite in the X-ray work of Whitaker and Jeffrey (1970). Some of the magnesium coordinated waters are said to have strong bonding with other atoms in the unit cell.

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REFERENCES

- KIGGINS, B., AND A. MANOOGIAN (1971) Electron spin resonance of Mn^{2+} impurities in blodite. *Can. J. Phys.* **49**, (in press).
- MANOOGIAN, A. (1971) A technique for correlating magnetic and crystallographic axes in electron spin resonance experiments. *J. Phys. E: Sci. Instrum.* **4**, 263.
- , AND A. G. DANILOV (1970) Electron spin resonance studies of Cr^{3+} impurities in soda alum. *Can. J. Phys.* **48**, 1448.
- PAULING, L. (1960) *The Nature of the Chemical Bond*. 3rd Ed. Cornell University Press. Ithaca.
- SIMANEK, E., AND K. A. MULLER (1970) Covalency and hyperfine structure constant A of iron group impurities in crystals. *J. Phys. Chem. Solids* **31**, 1027.
- SUTOR, D. J. (1967) The crystal and molecular structure of newberyite, $MgHPO_4 \cdot 3H_2O$. *Acta Crystallogr* **23**, 418.
- VINOKUROV, V. M., M. M. ZARIPOV, AND V. G. STEPANOV (1964) Paramagnetic resonance of Mn^{2+} in diopside crystals. *Soviet Phys. Solid State* (English Transl.) **6**, 870.
- , AND R. S. TUKHVATULLIN (1968) Electron paramagnetic resonance of Mn^{2+} ions in struvite. *Geokhimiya* (In Russian) **4**, 496.
- WHITAKER, A., AND J. W. JEFFERY (1970a) The crystal structure of struvite, $MgNH_4PO_4 \cdot 6H_2O$. *Acta Crystallogr.* **B26**, 1429.
- , AND ——— (1970b) X-ray evidence for a single-bonded rotating ammonium ion in struvite. *Acta Crystallogr.* **B26**, 1440.

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