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ESR SPECTRA OF Mn^{2+} IN HEAT-TREATED ARAGONITE

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ABSTRACT

Unheated aragonite samples from different locations, both of inorganic and organic origins, do not show Mn^{2+} ESR spectra, whereas calcite, including calcite transformed from aragonite, does show an Mn^{2+} spectrum. Single aragonite crystals show a different Mn^{2+} spectrum, but only after heating above 300°C. All powdered samples, after heating above 300°C, show the Mn^{2+} spectrum characteristic of calcite. There is a strong correlation between the intensity of the ESR Mn^{2+} spectrum characteristic of calcite and the amount of the calcite which has been transformed from aragonite, as determined by X-rays. It is suggested that there is a reaction of $Mn^{3+} \rightarrow Mn^{2+}$ occurring at temperatures above 300°C in aragonite crystals containing manganese.

INTRODUCTION

The polymorphic modifications of calcium carbonate, calcite, and aragonite have received a great amount of attention. Their transformation is complex and depends on many parameters, such as pressure, temperature, impurities, and grain size. The problem has recently been reviewed by Fyfe and Bischoff (1965). More recent work and references can be found in the publications of Boettcher and Wyllie (1968) and Taft (1967).

It is now well established that aragonite is metastable at room temperature. Aragonite transforms spontaneously into calcite at about 400°C as determined by Faust (1950); and at even lower temperatures under higher pressures. Fyfe and Bischoff show that certain ions inhibit the transformation to calcite, whereas other ions speed up the transformation. These authors indicate that ions which inhibit the growth of calcite by absorption or coprecipitation on the calcite cause aragonite to dominate. No study has been made of the effects of paramagnetic impurities on the transformation.

Most minerals contain a number of paramagnetic ions. Calcite, in particular, usually shows traces of divalent manganese. Mn^{2+} in calcite has been intensively studied by spin resonance techniques (Hurd *et al.*, 1954; Kikuchi, 1955; McConnell, 1956; Kikuchi *et al.*, 1960; Matarrese, 1961). No comparable study exists of Mn^{2+} in aragonite.

We have measured the paramagnetic resonance spectrum of Mn^{2+} in heat–treated aragonite, and its relation to the aragonite-calcite transition.

THEORY

In the calcite structure (space group $R\bar{3}c$) the calcium ions are surrounded by six CO_3^{2-} ions which form an approximate octahedron. The structure can be visualized as consisting of alternating planes of triangular CO_3^{2-} ions. These are two non-equivalent positions of the cations.

The spin Hamiltonian that corresponds to this symmetry is given by

$$\mathcal{H} = \beta \mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S} + B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^3 O_4^3 + (B_4^3 O_4^3)^* + \mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I} \qquad S = 5/2$$

B_n^m	are phenomenological crystal field parameters.
O_n^m	are operators which represent linear combination of Legendre polynonomials.
$\mathbf{g}$	is the tensor characteristic of the Zeeman splitting.
β	is the Bohr magneton.
$\mathbf{H}$	is the external magnetic field.
$\mathbf{S}$, $\mathbf{I}$	are the electronic and nuclear spins respectively.
$\mathbf{A}$	represents the hyperfine tensor.

The nomenclature is the usual one used in spin resonance. The most significant parameter is $D = 3B_2^0$, a measure of the axial splitting, and is of the order of 40 gauss. The parameter B_4^3 is very small and the complex number of $(B_4^3O_4^3)^*$ indicates the non–equivalence of the two cations. This shows up as doubling of the spectrum when the magnetic field is directed along an arbitrary axis. A and B, the components of the hyperfine interaction, are approximately equal and about 93.9 gauss, characteristic of the highly ionic character of calcium (Van Wieringen, 1955).

The spin resonance spectrum of Mn^{2+} in aragonite (space group $Pnma$) has not been measured previously. The immediate nearest neighbors of the calcium are 9 oxygen ions, of which 3 are bridging to adjacent calcium ions and 6 are non–bridging ions.

The structure has 4 cations per unit cell which are related to each other by screw axes and glide planes. We shall denote the crystallographic axes by a, b, c, and the magnetic axes by x, y, z. These two axes are related, as shown by experiment, by a rotation of the magnetic axes of 31° around b, so that y is left parallel to b. The x, z axes are in the a, c plane and make an angle of 31° with these. If the magnetic field is along the *b* crystallographic axis, all the ions are magnetically equivalent and one sees one pattern of the Mn^{2+} spectrum. If the field is along the *c* or *a* axes, there will be two distinct patterns, which will behave very differently from those found in calcite.

The spin Hamiltonian could, in principle, comprise all operators of the order 2 and 4, such as

$$\mathcal{H} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + B_2^0 O_2^0 + B_2^2 O_2^2 + B_4^0 O_4^0 + B_4^2 O_4^2 + B_4^3 O_4^3 + B_4^4 O_4^4 + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}.$$

In general, there are 30 permitted lines of $\Delta M = \pm 1$, $\Delta m = 0$ transitions; and many more forbidden lines of $\Delta M = \pm 1$, $\Delta m = \pm 1$, or $\Delta M = \pm 1$, $\Delta m = \pm 2$ transitions for each magnetically non-equivalent cation (Mankowitz and Low, 1970). For each ion per unit cell, the powder spectrum is an average of the angular dependence of the spectrum.

We shall assume in the following, and this is born out by experiment, that the fourth order parameters are small compared with the second order parameters.

The spectrum then can be approximated by the Hamiltonian

$$\mathcal{H} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + B_2^0 O_2^0 + B_2^2 O_2^2 + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} + \text{higher order terms.} \qquad (3)$$

We find experimentally that

$$3B_2^0 = D = 221 \pm 1 \text{ gauss}$$

$$B_2^2 = E \sim 49 \pm 2 \text{ gauss}$$

and, therefore, the fine structure separation is very different from that of calcite. The **g** tensor and **A**, the hyperfine tensor, are also slightly different from that of Mn^{2+} in calcite. Hence, the powder spectrum of Mn^{2+} in aragonite will differ from that of Mn^{2+} in calcite.

EXPERIMENTAL RESULTS

All spectra were taken on a Varian 3 cm spectrometer and at room temperatures. The spectrum of manganese in calcite (Iceland-spar) is shown in Figure 1 taken at room temperature and with the magnetic field directed along the magnetic *z* axis. Figure 2 shows the powder spectrum of manganese of the same crystal of calcite. The outer weaker lines in the powder spectrum are indicative of the fine structure (term $3B_2^0$ in the Hamiltonian). For very good crystals, such as those shown in Figure 1 and 2, all the lines are sharp and the line

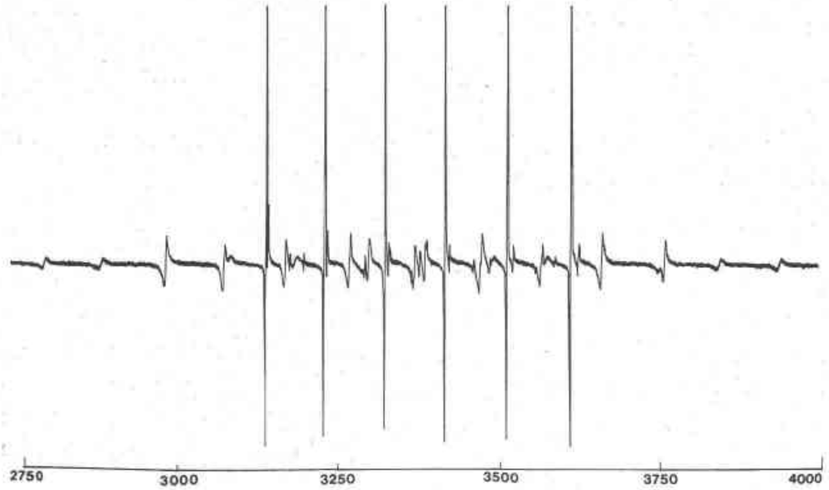

FIG. 1. The ESR spectrum of Mn^{2+} in single crystals of calcite (Iceland spar). The spectrum is taken at 3 cm wavelength and with the magnetic field parallel to magnetic z axis. The lines in Iceland spar are particularly sharp.

widths less than 1 gauss. For crystals of poorer quality, or with high Mn^{2+} concentration, or with Mn^{2+} in the presence of high concentrations of other paramagnetic impurities such as Fe^{3+}, the Mn^{2+} lines are either considerably broadened or superimposed on a large background

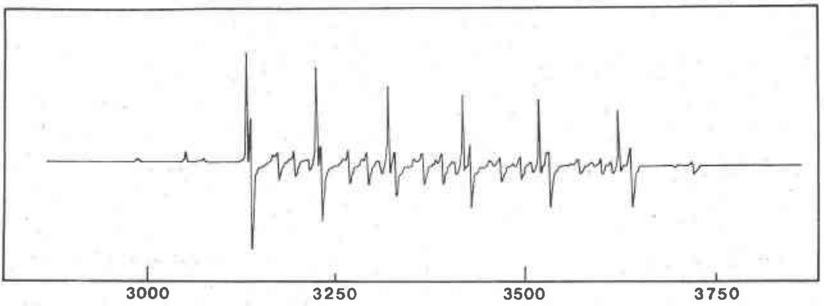

FIG. 2. The ESR spectrum of Mn^{2+} spectrum in powered calcite samples (Iceland spar). The six intense hyperfine lines correspond to the six strong hyerfine lines in Figure 1. It is to be noted that they are double. The doubling arises because of the magnetic inequivalences of the two ions. The weaker outer lines arise from the remnants of the fine structure lines shown in Figure 1. The main six hyperfine lines are shifted in Figure 2 from those of Figure 1, because of the different setting of the operating frequency of the spectrometer.

line. The outer lines are often washed out. We shall be concerned with the comparison of aragonite and calcite crystals, in which the background line is not very strong or is absent, and in which the manganese concentration is relatively small, in general less than 1 part in 10^4.

Aragonite single crystals were from Aragon, Spain; Sicily, Italy; and Somerset, England. Most of the work reported here was done on crystals from the first two localities. Powdered samples of aragonite were obtained either from these crystals, ground to fine powder (mesh 400), or from Tiran, Israel, or from coralline aragonite of recent *Acropora sp.* from Eilat, Israel. In addition synthetic aragonite was prepared by A. Starinsky of the Department of Geology, The Hebrew University. The aragonite was identified by its characteristic X–ray pattern. Powdered samples were put into standard quartz tubes, weighed, and inserted into a fixed length at the center of the cavity. None of the single crystals nor any of the powder showed any spin resonance spectrum at room temperature. Similarly, many of the other samples from different locations showed no detectable Mn^{2+} spectrum (less than 1 part per million). On the other hand all calcites obtained from various locations, including calcite crystals or powdered samples whose origin, according to petrological evidence (Schneidermann, 1969), is from the aragonite–calcite transformation, showed the distinct Mn^{2+} spectrum similar to Figure 1 or Figure 2.

On heating single crystals of aragonite to a temperature of 300°C for a few hours (about 4 hours, typically), a distinct spectrum appeared which can be described by equations 2 or 3 and is therefore

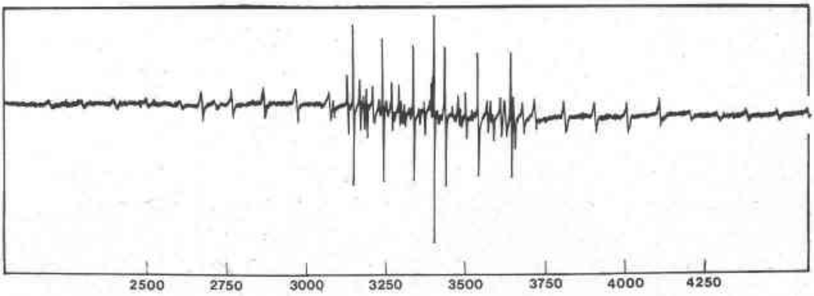

FIG. 3. The ESR spectrum of Mn^{2+} in single crystal aragonite (Aragon, Spain). The crystal was heated to 300°C for a few hours. The magnetic field is along the magnetic z axis. Compare with Figure 1. The spectrum consists of 60 lines; 30 lines spread over approximately 2,000 gauss and 30 lines fall approximately within the six intense hyperfine lines within 600 gauss.

assigned to Mn^{2+} (in aragonite) with the experimentally determined parameters mentioned above. The intensity of the spectrum depended on the time that the crystals were heated at 300°C. The spectrum is shown with the magnetic field along the magnetic z axis (Figure 3). It is clear that it differs considerably from that of calcite (see Figure 1). The spectrum is also shown along the crystallographic b axis, where all the cations are equivalent (Figure 4).

Detailed inspection of the spectra of powder prepared from previously heat–treated single crystals of aragonite and that of powdered calcite show the following differences: (a) in the position of the weaker outer lines, characteristic of the fine structure; (b) in the separation of the doublets, characteristic of the existence of two non–equivalent sites; (c) in a slightly different spacing of the six main hyperfine lines; and (d) in a small shift of the center of gravity of the spectrum which arises from a difference in the g factors.

The single crystal spectrum is consistent with the Hamiltonian in equation (3). One can, therefore, conclude that the spectrum is due to Mn^{2+} in aragonite. The angular dependence of the 30 lines and the existence of only two non–equivalent sites is strong evidence that the Mn^{2+} takes the place of the Ca^{2+} in aragonite. X–ray analysis indicated that no calcite was present in the heated aragonite samples.

Heating single crystals to temperatures above 380°C caused disintegration of the crystal. Most probably the onset of the phase transformation was the cause of the disintegration.

When the powdered aragonite sample (either untreated crystals that were ground to powder or natural powdered samples) were heat treated, the Mn^{2+} spectrum typical of calcite powder samples was generally obtained. Standard samples were prepared and heated to different temperatures. Below 300°C, no Mn^{2+} was observed and X–ray analysis did not show any transformation to calcite. From 300°C to 450°C, the Mn^{2+} spectrum of calcite was observed. The intensity of the spectrum depended on the temperature to which the powder was heated. The spectrum of Mn^{2+} in aragonite was also present at 300°C but was relatively weak. When heated for only a few minutes to 400°C or higher, the calcite spectrum reached nearly a maximum intensity. X–ray analysis indicated that a large fraction of aragonite had transformed to calcite, roughly in proportion to the intensity of the manganese ESR signal. Further heating slowly increased the calcite concentration and the intensity of the Mn^{2+} spectrum.

Since it is difficult to heat a standard sample to different temperatures for a fixed time, because of the time lag in the heating process, we measured the calcite concentration and the ESR signal height of

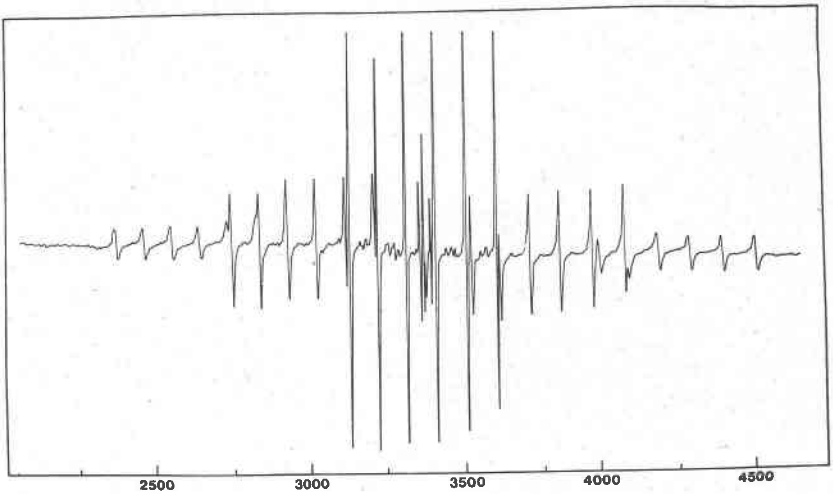

FIG. 4. The ESR spectrum of Mn^{2+} in aragonite with the magnetic field along the crystallographic *b* axis. Note that all the inequivalent sites coincide and only 30 lines are to be seen.

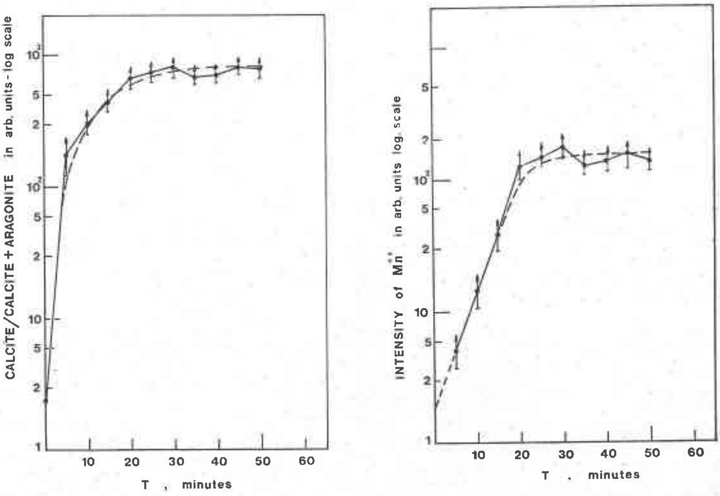

FIG. 5. (a). The concentration of calcite, as determined by X-rays in aragonite samples, as a function of heating time at 430°C. (b). The intensity of the Mn^{2+} spectrum as a function of heating time. Notice that both curves show saturation behavior at approximately the same time. The dotted curves are an average through the experimental points.

Mn^{2+} for different heating times when the samples were kept at a constant temperature of 430°C. Figures 5a and 5b show the intensity[1] of the ESR spectrum (an arbitrary scale) and the calcite concentration as a function of the time. A comparison of these two figures shows a striking resemblance, although the curves are not quite identical. Both curves indicate that after 20 minutes, the amount of calcite and the amount of Mn^{2+} reached saturation. Further heating slowly increased the concentration of calcite. The intensity of the ESR spectrum, however, did not increase significantly.

The same behavior was obtained for aragonite samples of organic origin. The only difference was the slightly greater linewidth in the Mn^{2+} calcite spectrum. This is evidence for the poorer quality of the calcite crystals.

DISCUSSION

There are several significant aspects of this study which we would like to summarize:

(a) Aragonite single crystals or powders of inorganic origin do not show any ESR Mn^{2+} spectrum, whereas most calcite samples do show a distinct Mn^{2+} spectrum.

(b) Aragonite single crystals heated to a temperature below the phase transformation show a distinct and characteristic Mn^{2+} spectrum, very different from that of Mn^{2+} in calcite.

(c) The phase transformation from aragonite to calcite can be observed by noting the change in intensity of the two distinct Mn^{2+} spectra. In powders the ESR spectrum characteristic of calcite is already observed at 300°C, at a lower temperature than in single crystals. The amount of Mn^{2+} as inferred from the intensity of the Mn^{2+} ESR spectrum in heat-treated powders is similar but not identical to the concentration of calcite which has been transformed from aragonite at a given temperature. The remaining aragonite has only a small background intensity of Mn^{2+} signal.

(d) Calcite that, according to petrological evidence, (Schneidermann, 1969), has been formed from aragonite at relatively low temperatures, (probably not a solid state transformation[2]) shows a typical Mn^{2+} calcite spectrum.

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[1] The accuracy of the intensity measurement of the ESR spectrum was probably about 20 percent. Problems connected with intensity measurements have been summarized by Poole (1963).

[2] We have some evidence that calcite that is transformed from aragonite in a $CaCl_2$ water solution at 40–70°C shows the typical Mn^{2+} calcite spectrum. However, only the initial and end products were investigated and further experiments are necessary.

The main question is where the Mn^{2+} comes from. Manganese must be already present in the aragonite. We conjecture that Mn^{3+} may be present in the aragonite, probably substitutionally for the Ca^{2+} site. Mn^{3+} has the ground state of d^4, ${}^5D_4$. At such low symmetry the levels consist of five singlets with a separation of several to a few hundred cm^{-1}, so that no ESR spectrum can be detected. At higher temperatures we conjecture that an additional electron is trapped to form Mn^{2+}. A possible reaction is

$$\mathrm{Mn}^{3+} + e^- \rightarrow \mathrm{Mn}^{2+} \tag{4}$$

Obviously it would be important to measure the electrical conductivity of aragonite as a function of the temperature. The extra electron may originate from a charge compensating (possibly monovalent) ion, or from an electron in a vacancy, which is released at higher temperatures.

In powder samples, the transformation of aragonite to calcite and the creation of Mn^{2+} go hand–in–hand because of the relatively low temperature at which the calcite is formed. It is not clear from our results whether these are independent processes or whether the transformation aids in the creation of the Mn^{2+} spectrum.

Our results indicate the importance of investigations of synthesized single crystals of aragonite containing manganese impurities. One has to find out what the parameters are that stabilize the Mn^{2+} spectrum in aragonite. Further measurements on aragonite containing Mn^{2+} or Mn^{3+}, at various pressures and temperatures as well as in the presence of other impurities, are important. Such measurements help determine to what extent the impurities such as manganese may be connected with the phase transformation.

In addition to the Mn^{2+} spectrum we observed weaker and complicated spectra near $g = 2.00$ which may be related to some radiation damage, possibly CO_2^- molecule ions, in some aragonite samples. The spectrum is similar to that observed by Marshall *et al.* (1963) for calcite. This will be described separately.

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