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*Radiation
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EXPERIMENTS ON COLOR CENTERS IN
CRESTMORE BLUE CALCITE

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UNIVERSITY OF CALIFORNIA
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EXPERIMENTS ON COLOR CENTERS IN
CRESTMORE BLUE CALCITE

Alice Wiersema
(M.S. Thesis)

December 9, 1960

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Berkeley, California

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ABSTRACT

Color centers in blue calcite from the Crestmore region of California were studied by electron spin resonance. A spectrum of four equally spaced lines is obtained in addition to the spectrum of thirty lines due to manganese. This quartet extends over a range of about thirty gauss and is centered about a g value of 2.013. The spectrum of powdered calcite shows a variation of line width with magnetic field. By using the theory of McConnell--which relates the paramagnetic relaxation times, T_1 and T_2 , the hyperfine interaction, and the correlation time, τ_c with the anisotropy of the g value-- Δg is calculated as 0.002. From thermoluminescence studies of the blue calcite three glow peaks are obtained, at 52° , 170° , and 262°C . The peak at 262°C is obtained only with blue calcite. It occurs at the temperature at which the sample bleaches, and is related to the color centers. Spectrochemical and quantitative chemical analyses were made to determine what impurities are responsible for the color centers. From consideration of the spectroscopic g value and the hyperfine splitting it is probable that the color centers are due to a cationic impurity with nuclear spin $3/2$.

I. INTRODUCTION

The electron spin resonance of color centers in blue calcite was first studied by L. R. Doyle.¹ He found that when a crystal of this mineral was cooled to -150°C a spectrum was obtained consisting of a nearly isotropic quartet with a g value somewhat greater than the value for a free electron. This quartet disappeared when the sample was bleached by heating, but the color and the quartet could be regenerated by x rays. He proposed a model for the color center consisting of Fe^{++} and Be^{++} impurity ions occupying adjacent calcium ion sites in the calcite lattice.

Deposits of blue calcite are found in the Crestmore region of California, and always occur in or near great masses of contact rock. The samples used in this study are from the Sutro collection sample No. 55 and were obtained from Dr. Adolf Pabst, professor of mineralogy at the University of California, Berkeley.

Many speculations have been made as to the cause of the blue color in this mineral. A study of the linear thermal expansion of blue calcite and white calcite was made by Rosenholtz and Smith.² They found a high value for the coefficient of linear expansion for the blue calcite, which is correlated with a high stress history. They concluded that the blue color was due to residual strain which is relieved by heating.

A study of the effects of gamma radiation and experimental deformation on calcite by Handin et al.³ showed that by compression of white calcite parallel to the C_v axis, producing translation gliding, and subsequent gamma irradiation of the sample, a deep ultramarine blue color was produced.³ The same effect could be produced by similarly compressing previously irradiated calcite samples. Compression perpendicular to the C_v axis had no such effect. Their conclusion was that translation gliding generates charge vacancies by dislocation, thus accounting for the presence of color centers. They also studied the thermoluminescence of these samples and found that translation gliding produces a new glow peak at 280°C , in addition to the three peaks at 120° , 240° , and 310°C found in white calcite.

There have been some studies made on other types of color centers in calcite. J. C. Kemp has made a study of the color centers produced by fast neutron bombardment of calcite at liquid helium temperatures.⁴ A complex spectrum was obtained of highly anisotropic lines believed to be due to several different types of color centers. A study by J. L. Burckhardt of color centers produced by irradiating calcite with 3-Mev electrons showed a spectrum of seven anisotropic lines.⁵ It was found that these color centers were stable only at low temperature, fading in a few hours at room temperature.

This study is concerned with the naturally occurring stable color centers in blue calcite. This work was undertaken in an effort to learn more about these color centers by a study of the angular dependence, temperature effects, and effects of bleaching and irradiation on the electron spin resonance spectrum of the quartet in this crystal. Thermoluminescence studies were made in order to learn about the electron traps in the crystal, and chemical analyses of white and blue calcite samples were made to discover what impurities may be responsible for the color centers.

II. ELECTRON SPIN RESONANCE

A. Theory

A theory of the electron spin resonance as applied to ions in crystals can be stated briefly. Paramagnetism is distinguished from diamagnetism by the presence of permanent magnetic dipoles produced by the electron's orbital motion plus its spin. Permanent magnetic dipoles occur whenever an atom or an ion contains a partly filled electron shell. This limits paramagnetism to a small number of elements--the transition metals and the rare earths.

For an isolated atom, the spin vector and the orbital angular momentum vector are coupled by spin-orbit interaction, which is usually stronger than the interaction with the applied field. For the transition metals the interaction between the electron and the field produced

by the diamagnetic ions in the crystal is large enough so that the orbital motion of the electrons is quenched, and the magnetic properties of these salts corresponds to spin-only magnetism.⁶

When a magnetic field is applied to an ion with a resultant angular momentum, the spin angular momentum vector can be considered to precess about the axis of H with an angular frequency, $\omega = g \left(\frac{e}{2mc} \right) H$, where g is known as the spectroscopic splitting factor. It has a value of 2.0023 for a free electron.

This same equation can be derived from quantum-mechanical consideration of the magnetic dipole transitions between levels corresponding to different spatial orientations of J , the resultant angular momentum. In a magnetic field, H , these levels have energies equal to $Mg\beta H$, where M is the electronic magnetic quantum number. The transitions are governed by the selection rule $\Delta M = \pm 1$. Quanta of frequency $h\nu = g\beta H$ can induce transitions between these states. Since $\beta = eh/4\pi mc$, this expression is identical with the one above for the angular frequency.

When a system is in thermal equilibrium with its surroundings, the lower states have a greater population than the upper. The application of resonance radiation results in a more equal population of the different levels because the transitions up and down have equal a priori probability. The resonance absorption can be detected by the loss of energy from the radiation field as a result of these transitions.⁷

If the nucleus of a paramagnetic ion possesses a magnetic moment, hyperfine interaction is observed in the spectrum. This arises from the magnetic interaction of the electron with the nuclear magnetic moment. The nuclear orientation is quantized and the projection of the nuclear moment has $2I + 1$ orientations with respect to the electronic moment. The electronic levels are thus split into $2I + 1$ levels which are approximately equally spaced in a strong magnetic field. The allowed transitions between these levels are those for which $\Delta M = \pm 1$ and $\Delta m = 0$, resulting in a hyperfine structure of $2I + 1$ lines. Since all nuclear orientations have essentially equal probability at room temperature, the hyperfine lines due to a single nucleus will be of equal intensity.⁸

B. Experimental Procedure

The single crystals used for the electron spin resonance studies were cleaved along the natural rhombohedral cleavage planes to a size of about 3 mm on each side, the samples weighing from 50 to 60 mg. Each crystal was mounted on the end of a narrow glass rod and oriented visually so that the c-crystallographic axis was perpendicular to the axis of the glass rod. The glass rod was inserted in a holder with a graduated dial in order that the sample could be rotated with respect to the externally applied magnetic field and the angle of rotation measured.

When studies were made below room temperature, the sample was placed inside a vacuum-jacketed quartz tube and was cooled by means of cold nitrogen gas, generated by boiling liquid nitrogen from a 25-liter dewar. The temperature of the sample could be varied from room temperature to -150°C by adjusting the rate of flow of the nitrogen through the quartz tube. The temperature was measured by means of a copper-constantan thermocouple attached directly to the sample.

The electron spin resonance studies were carried out with a conventional microwave system similar to that described by Low.⁹ A rectangular brass cavity with a dominant mode of TE_{011} was placed in the magnetic field obtained from a Varian magnet and magnet power supply. An oscillating 100-cps modulating field was superimposed on the dc magnetic field and the modulation was varied from 0.5 to 2.5 gauss. The source of microwaves was a Varian V 58 klystron, contained in a Laboratory for Electronics stabilized oscillator unit. In these studies its frequency was approximately 8710 Mc/sec. The reflection from the microwave cavity was detected by a crystal diode. The power level at the crystal detector could be adjusted to an optimum by use of a magic tee bridge circuit. The magnetic field was swept through the resonance of the sample, the rate of sweep being variable over a wide range. The derivative of the absorption of the sample resonance was plotted automatically with a Leeds and Northrup recorder.

A study of the anisotropy of the lines was made by rotating the crystal in the field in increments of 45 degrees, and measuring the positions of the lines at these various angles. A proton resonance spectrometer was used to measure the magnetic field. A proton probe consisting of a dilute copper sulfate solution in a glass tube wrapped with a coil of copper wire was placed in the magnetic field, which was being swept through the resonance of the sample. The proton resonance spectrometer was tuned to the nearest harmonic of a 100-kc standard-frequency oscillator, and when the proton resonance peak crossed the center of the oscilloscope on which it was displayed, the pen was triggered to place a marker pip on the recorder plot. The spectrometer was then retuned to the next harmonic and the procedure repeated. By this means the field was marked every 100 kc, or 23.49 gauss. Because there was space inside the cavity only for the quartz Dewar and the sample of calcite, the proton probe was placed outside the cavity, but as near to the center of the field as possible. The resulting difference of 2 to 3 cm between the position of the sample and the proton probe in the magnetic field may have caused small but consistent errors in the field measurements.

No absolute measurements of the field were made. In order to determine the g value of the quartet, a comparison was made between the position of the quartet and the resonance spectrum of a sample of DPPH placed directly on the calcite sample.

C. Experimental Results

At room temperature the electron spin resonance of the blue calcite crystals was found to be identical with the manganese spectrum observed by Kikuchi and Matarrese.¹⁰ The spectrum consists of thirty lines extending over a range of about 1,000 gauss, depending upon the angle of orientation of the c -crystallographic axis with the applied magnetic field. There are six major lines, each about 3.5 gauss wide, due to the $M_{-1/2} \rightarrow M_{1/2}$ transition, and six peaks each corresponding to the four remaining transitions ($M_{-5/2}$, $M_{-3/2}$, etc.)

In addition to these thirty manganese lines, when the sample was cooled to -150°C by use of the liquid nitrogen apparatus previously described, four lines appeared between the two central $M_{-1/2} \rightarrow M_{1/2}$ transition manganese lines (see Fig. 1). These quartet peaks were of intensity approximately equal to the major manganese peaks. The integrated spectrum is shown in Fig. 2 for comparison of the relative intensities.

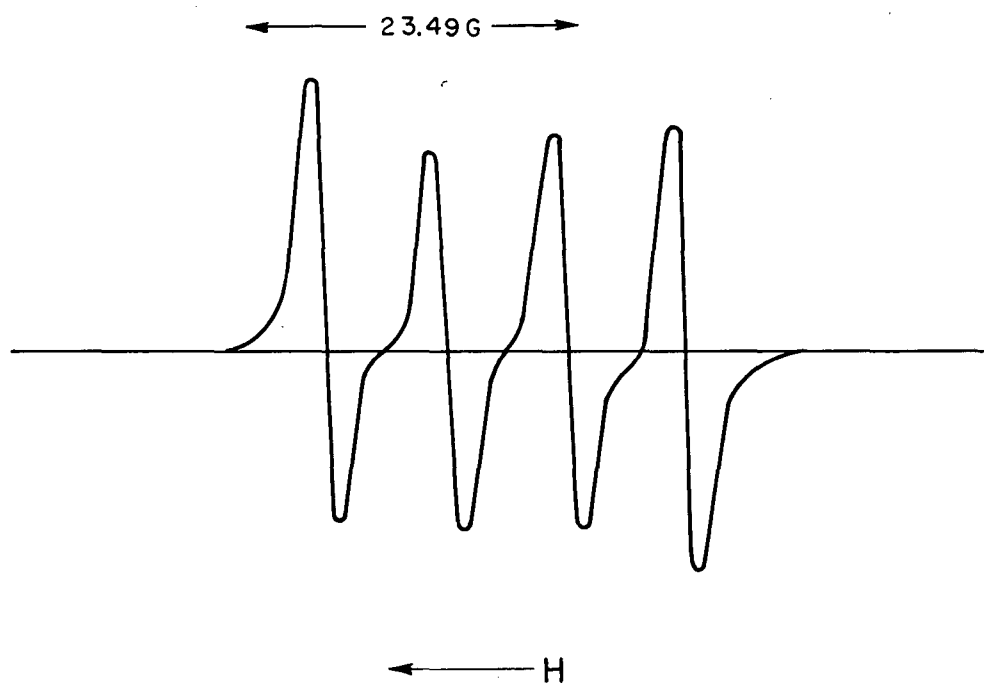
The width of each of the lines in the quartet, defined as the separation between the maximum and minimum points on the derivative of the absorption curve, was determined by measuring the magnetic field with the proton resonance spectrometer. The width of these lines was found to vary by as much as 0.5 gauss at different orientations of the crystal in the field, owing to the interference of the Mn lines in the spectrum, but the average of many different measurements gave widths for each line of from 2.0 to 2.5 gauss. The distance between the lines was found to be approximately 9.0 gauss, the whole quartet spectrum extending over a range of 30 gauss.

The g value for the quartet was found by comparing the position of the center of the quartet with the position of the resonance line of DPPH, the g value of the DPPH being assumed to be 2.0036 (see Fig. 3). Then by means of the formula

$$\Delta g = \frac{-\Delta H}{H_{\chi}} g_0$$

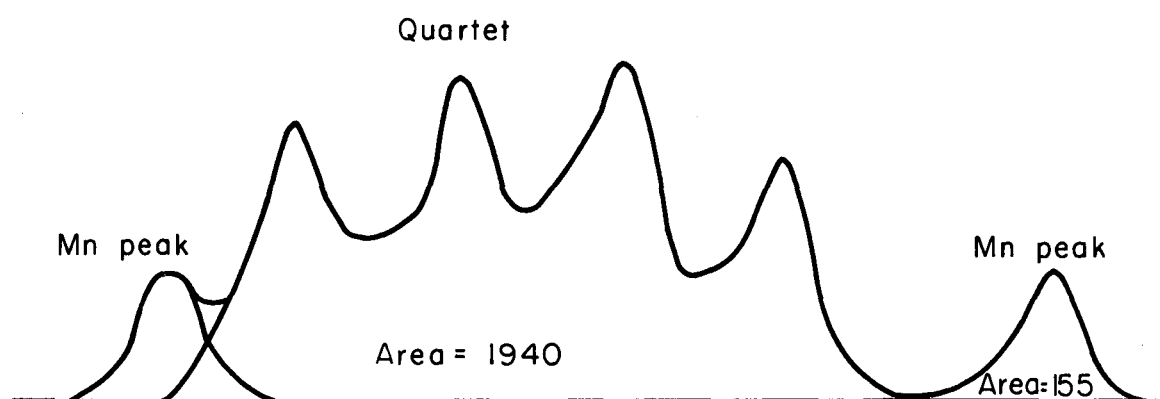
the g value was calculated as 2.013.

From the measurements of the position of the quartet as a function of angle, there appeared to be no anisotropy of the g value of the quartet, but in order to check this more closely, the quartet was observed in a powdered sample of calcite. The calcite crystal was irradiated with ultraviolet light in order to increase the intensity of the quartet with respect to the Mn lines. It was then powdered into very small fragments by use of a mortar and pestle and placed in a thin-walled glass tube. The electron spin resonance was first measured at room temperature to find out the position of the Mn lines, and then



MU-22253

Fig. 1. Derivative of the absorption spectrum of the quartet in blue calcite. H = magnetic field.



MU - 22255

Fig. 2. Integrated derivative of absorption spectrum of quartet and M_n line in blue calcite.

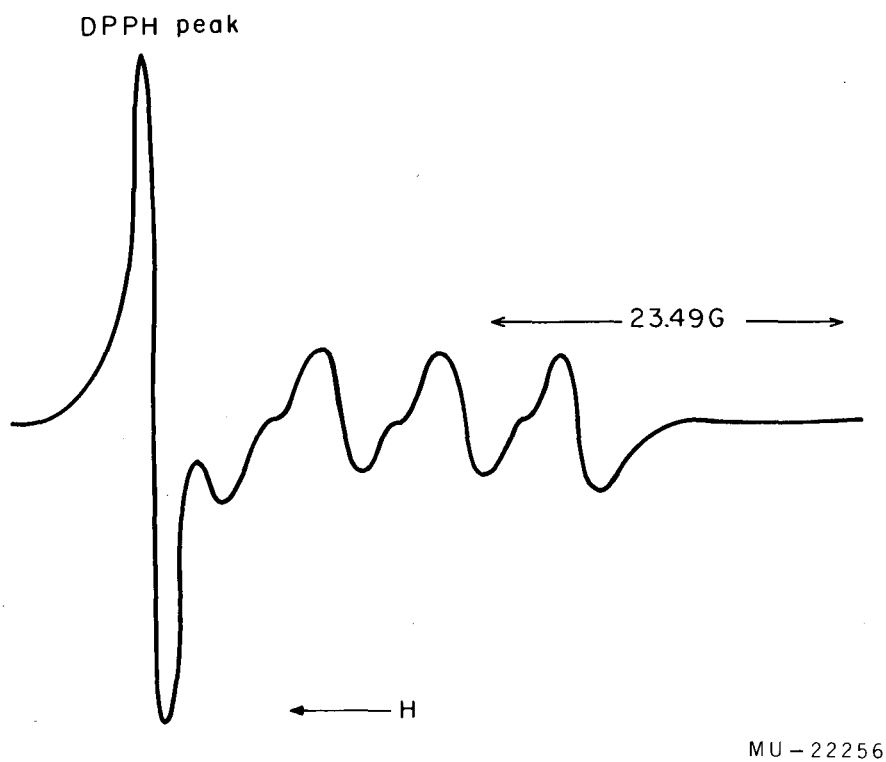


Fig. 3. Derivative of absorption spectrum of quartet and DPPH in blue calcite. H = magnetic field.

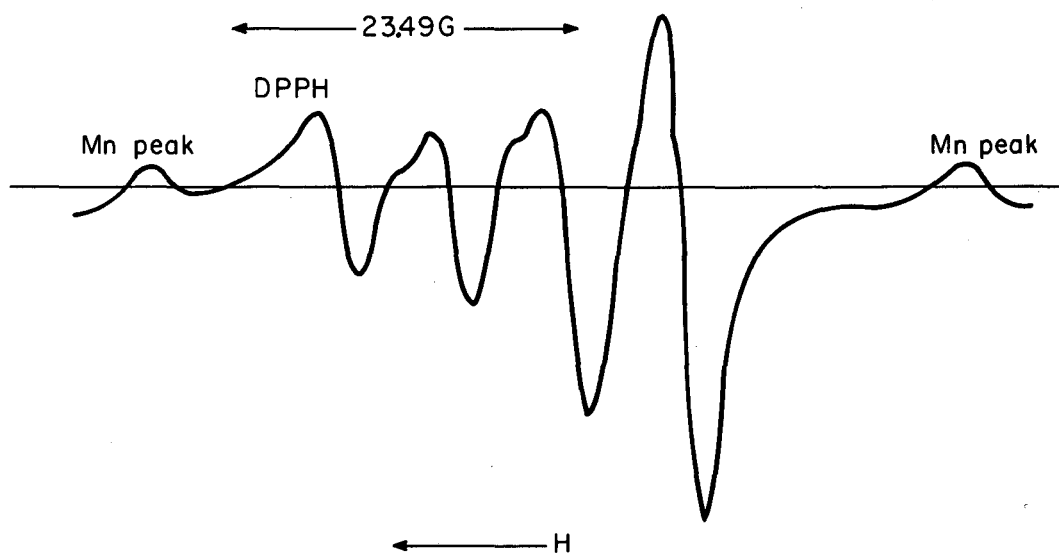
cooled to -150°C to observe the quartet. The spectrum obtained in this way is shown in Fig. 4.

The samples of calcite were bleached by heating on a copper block which was covered with a glass plate so they could be observed during the heating process. The samples began to lose their color at 225°C and were completely decolorized by 300°C . The electron spin resonance spectrum was taken of a bleached crystal for comparison with the spectrum of naturally blue calcite, and it was found that the quartet had disappeared, and the spectrum was identical to that of the manganese spectrum in blue calcite at room temperature.

The bleached samples could be recolorized by the use of a General Electric A H-4 mercury lamp from which a portion of the pyrex outer envelope had been removed. The samples were placed directly in front of the lamp and irradiated for periods of several hours. The blue color could also be regenerated by irradiation with x rays. A molybdenum tube was used, and the source was operated at 45 kv and 20 ma. It was found that the electron spin resonance spectrum of calcite recolorized by either of these methods was the same as that of the naturally blue calcite, thus establishing an apparent relationship between the blue color and the appearance of the quartet in the electron spin resonance spectrum.

D. Discussion of Electron Spin Resonance

The results of the electron spin resonance experiments can be summarized as follows. When a blue calcite crystal is cooled to -150°C , a quartet is obtained of approximately the same intensity as the manganese lines. This set of four lines is nearly isotropic and has an average g value of 2.013, somewhat greater than the g value for a free electron. The width of the lines is from 2.0 to 2.5 gauss, and the distance between them is about 9 gauss. The quartet spectrum disappears when the blue color is bleached by heating to 300°C , and can be produced again by recolorizing the sample with either ultraviolet light or x rays.



MU - 22254

Fig. 4. Derivative of absorption of ESR spectrum of quartet in powdered calcite at -150°C .

Since the quartet consists of four lines of approximately equal spacing and equal intensity, it seems probable that they are a result of hyperfine interaction of a nuclear spin of $3/2$.

The spin Hamiltonian for isotropic interactions is given as

$$\mathcal{H} = g\beta H \cdot S + AS \cdot I,$$

in which $AS \cdot I$ is the operator in the Hamiltonian representing the magnetic hyperfine interaction. For $S = 1/2$, $I = 3/2$, $H \parallel z$, and $g\beta H \gg A$, the electronic level corresponding to $M = +1/2$ has energies of $1/2 g\beta H + 1/2 A m$, where the nuclear magnetic quantum number, m , can take values of $3/2$, $1/2$, $-1/2$, and $-3/2$. The $M = -1/2$ level has energies of $-1/2 g\beta H - 1/2 A m$. The selection rules for the transitions are $\Delta M = \pm 1$, $\Delta m = 0$, so that the spectrum consists of $2I + 1 = 4$ lines with equal spacing A . The value for A for the color centers in blue calcite was found to be 9 ± 1 gauss.

The elements that have abundant isotopes of spin $3/2$ are given in Table. I.

Table I. ¹¹ Isotopes of nuclear spin $3/2$ with more than 80% natural abundance.

Isotope	Natural abundance %	Isotope	Natural abundance %
Li ⁷	93	Br ⁷⁹	51
Na ²³	100	Br ⁸¹	49
K ³⁹	93	Ga ⁶⁹	60
Be ⁹	100	Ga ⁷¹	40
B ¹¹	81	As ⁷⁵	100
Cu ⁶³	69	Tb ¹⁵⁹	100
Cu ⁶⁵	30	Ir ¹⁹¹	40
Cl ³⁵	75	Ir ¹⁹³	60
Cl ³⁷	25	Au ¹⁹⁷	100

For elements that have two isotopes, each with spin $3/2$, i. e., Cu, Cl, Br, Ga, and Ir--there would be a splitting of the hyperfine structure if the two isotopes had magnetic moments that differed appreciably from each other, but in all these cases the magnetic moments are sufficiently close in value that this might not be observed.

The g values for various paramagnetic centers are as follows:

F centers in KCl ¹²	1.995
V centers in KCl ¹³	2.002 to 2.042
Cu ⁺⁺ in cubic field ¹⁴	2.0 to 2.5
Cu ⁺⁺ in trigonal field ¹⁵	2.1 to 2.5
Fe ⁺⁺⁺ in glass ¹⁶	0.5 to 10
Mn ⁺⁺ in calcite ¹⁷	2.002
Free electron	2.0023

It has been shown that an electron deficiency (hole)--as in V-type centers in alkali halide crystals--always gives a g value larger than the free-electron g value, whereas in F centers, which are caused by electrons in anion vacancies, the g value is smaller. The difference is due to the sign of the spin-orbit interaction in the spin Hamiltonian. The shift in the g value for the quartet is +0.01, indicating that it is a result of an electron deficiency or hole. Seitz¹⁸ has proposed a model for the V center in alkali halide crystals which is the antimorph of an F center. It consists of a cation vacancy surrounded symmetrically by a hole. There is thus an excess of the halide ion present in the crystal, and because of the strong tendency of halide ions to form covalent bonds, the V center is considered to be composed of molecule ions of the type Cl₂ - or Cl₃ -. It is difficult to see how this type of model could be used to explain the color centers in the calcite crystal.

Of the list of isotopes of spin $3/2$ those most likely to occur naturally in this mineral are Na, Li, K, Cu, Cl, Br, and Au. Of these, only Cu⁺⁺, Au⁺⁺, Cl, and Br would give the positive shift of g value observed.

The concentration of halide ion, however, is insufficient to account for the spectrum which is of intensity equal to the manganese spectrum. A quantitative analysis on the sample has shown a halide ion concentration of 0.007 mole %, as compared to a manganese concentration of 0.03 %.

The probable explanation for the observed spectrum consists of an ion of a transition group with a nuclear spin of $3/2$ substituting for calcium in the calcite lattice.

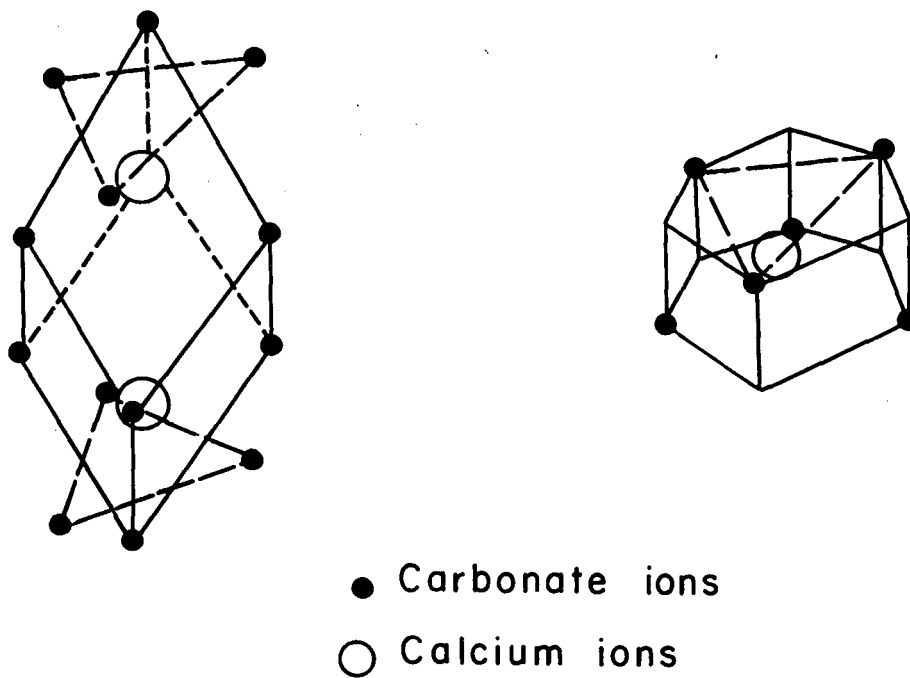
The structure of calcite is cubic, distorted by compression along one triad axis. A diagram of a rhombohedral unit cell is shown in Fig. 5. A divalent ion substituting for calcium would be in a field of trigonal symmetry. In a study of $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$ it was found that cupric ion in a trigonal field can give an isotropic g value.¹⁹

There are, however, certain difficulties in ascribing the quartet to cupric ion. The magnitude of the shift in g value found in this study is much smaller than has been found in other crystals for Cu^{++} . For copper ion in various trigonal crystals the values have been found to be between 2.1 and 2.5, while the g value for the quartet was only 2.013.

Another difficulty is the magnitude of the hyperfine splitting. For most transition-group ions in crystals the value is between 10^{-1} and 10^{-3} cm^{-1} . For copper ion in a trigonal field it was found to be greater than 1×10^{-3} in all cases, as compared with 8×10^{-4} found for the quartet in blue calcite.²⁰

These same difficulties would also apply to Au^{++} as the paramagnetic center. The g value of the idthiocarbamate of Au in solution has been found to be 2.040 and the hyperfine splitting $2.8 \times 10^{-3} \text{ cm}^{-1}$.²¹

A quantitative chemical analysis for Cu shows it to be in insufficient concentration (as compared with manganese ion) to account for the color centers. A value of 0.003 mole % was found by a colorimetric analysis (Appendix B). However, this analysis did not agree with the spectrochemical analysis on the sample, which showed a Cu ion concentration of 0.03%, which is the same as the mole % of manganese ion.



MU - 22257

Fig. 5. Diagram of unit rhombohedral cell in calcite.

ion. It is felt that the colorimetric analysis is the more accurate one, but this analysis should probably be checked by another method.

The electron spin resonance spectrum of the powdered sample can be explained by consideration of the effects of the anisotropy of the g value on the line width. McConnell²² has developed a theory in which the anisotropy can be related to the paramagnetic relaxation times, T_1 and T_2 , the hyperfine interaction, $A - B$, and τ_c , the correlation time describing Brownian tumbling motion of a microcrystal in the liquid state. He derived the following formula:

$$\left(\frac{1}{T_2} \right)^2 \approx \frac{32\pi}{45} \frac{(\Delta g \beta H_0 + b I_z)^2}{h^2} \tan^{-1} \frac{2\tau_c}{T_2} \quad (1)$$

For a crystal, τ_c can be assumed to be very large, so that one has

$$\tan^{-1} \frac{2\tau_c}{T_2} = \frac{\pi}{2}$$

Then

$$\frac{1}{T_2} \approx \sqrt{\frac{32}{90}} \pi \frac{(\Delta g \beta H_0 + b I_z)}{h} \quad (2)$$

The line width, $\Delta \nu$, is related to the relaxation times T_1 and T_2 by the expression

$$\Delta \nu \approx \frac{1}{\pi T_2} + \frac{1}{2\pi T_1} \quad (3)$$

Since the contribution of the anisotropic hyperfine interaction to paramagnetic relaxation depends on I_z , different hyperfine multiplets show different line widths.²³

For a crystal, T_1 is large, so that the second term is negligible. By a combination of Eq. (2) and (3), the relationship between $\Delta \nu$, Δg , and b is obtained:

$$\Delta \nu \approx \frac{1}{\pi T_2} \approx \frac{1}{h} \sqrt{\frac{32}{90}} (\Delta g H_0 + b I_z)$$

In the powdered spectrum of calcite it can be seen that if Δg and b have the same sign there is an increasing line width as I_z increases. On the assumption that the width of the lines is proportional to the height of the peaks in the derivative curve, the ratio of the widths of the lines corresponding to $I_z = 3/2$ and $I_z = -3/2$ is found to be approximately 2 to 1. From this value the relationship of Δg to b can be calculated as follows:

$$\Delta g \beta H_0 - \frac{3}{2} b \approx 2(\Delta g \beta H_0 + \frac{3}{2} b),$$

$$2\Delta g \beta H_0 \approx \frac{9}{2} b, \text{ or } b = \frac{4}{9} \Delta g \beta H_0$$

From the line widths,

$$\Delta g \beta H_0 \approx .2 \text{ gauss},$$

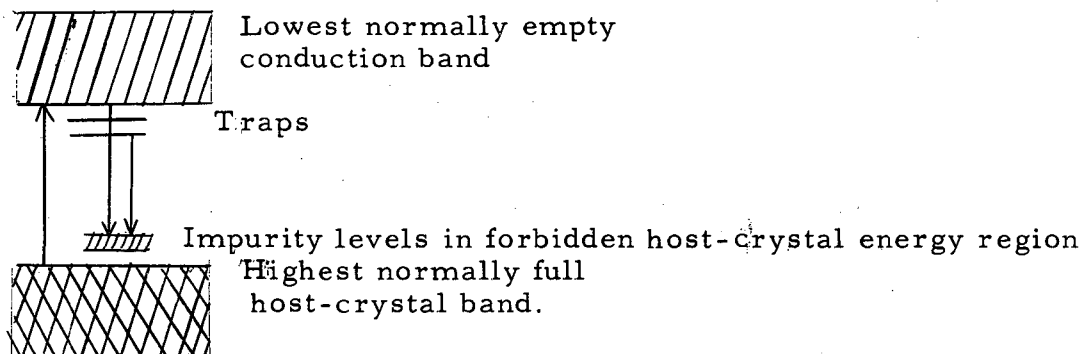
Then $\Delta g \approx 0.002$.

From these results it is clear that the quartet is not exactly isotropic, although these deviations are very small in single crystals. It is still possible but not very probable that either Cu^{++} or Au^{++} is responsible for the quartet. If these ions are the source of the quartet, it is not known what could cause the disappearance of the quartet after the crystals are heated. The origin of the quartet is still undetermined.

III. THERMOLUMINESCENCE

A. Theory

Phosphors are materials that absorb quanta of energy from primary excitant particles and convert a portion of the absorbed energy into detectable photon emission. The possible energy changes accompanying luminescence are illustrated by the energy-level diagrams of valence electrons as presented by Leverenz.²⁴



Excitation occurs by the process of a primary particle giving up some or all of its energy to raise electrons from occupied levels to unoccupied levels in the conduction band. The excited electron in the conduction band tends to lose energy rapidly to the crystal, until the energy of the electron has been reduced so that it occupies a level near the lower edge of the conduction band. At this point, the excited electron has very little kinetic energy and may drop into an unoccupied level introduced by an un-ionized impurity, or become trapped in a lattice imperfection.

Impurities which act as traps are generally multivalent cationic impurities known as activators, and the trapping process involves a change in the effective valence of the impurity ion. The luminescence associated with a particular impurity is found to be highly dependent

on the environment. In some cases the activators are nonluminescent in their own pure compounds in solid form, whereas appreciable luminescence is obtained when the luminescence centers are in a crystalline matrix of a host crystal.²⁵

Curves of luminescent output as a function of temperature are called glow curves. If traps are filled by excitation at low temperature, they may be emptied by raising the temperature, the release of electrons being accompanied by a characteristic activation energy.

The manner in which energy is released from trapping centers at different temperatures indicates the depth of the traps, higher temperature peaks corresponding to greater trap depth. The thermal trap depth (in electron volts) is related to the temperature of maximum glow by the approximation

$$E \approx 30 kT_g,$$

where k = Boltzmann's constant, and T_g = the absolute temperature of maximum glow.²⁶ This expression comes from $\nu_a e^{-E^*/kT}$

the probability per unit time of thermal emptying of traps, in which electrons make ν_a attempts to escape per second. ν_a is of the order of the highest vibration frequency of atoms in the crystal.

B. Experimental Procedure

The apparatus used for the glow-curve studies on blue calcite was similar to that described by Medlin.²⁷ The samples were ground into a fine powder with a mortar and pestle and placed directly on a copper block. The copper block was heated by means of a coil of asbestos-covered chromel wire; the rate of heating could be controlled by varying the current. In most cases the samples were heated at the rate of approximately 1° per minute from room temperature to 360°C . The temperature was measured by a thermometer which was inserted into the interior of the copper block directly below the sample. A 5819 photomultiplier tube used for detecting the luminescence was housed in

an aluminum tube which was placed over the copper block, separated by a section of transite for insulation. A solution of copper sulfate was used as a filter between the copper block and the photomultiplier. The signal from the photomultiplier was automatically plotted by a Brown recorder.

C. Results

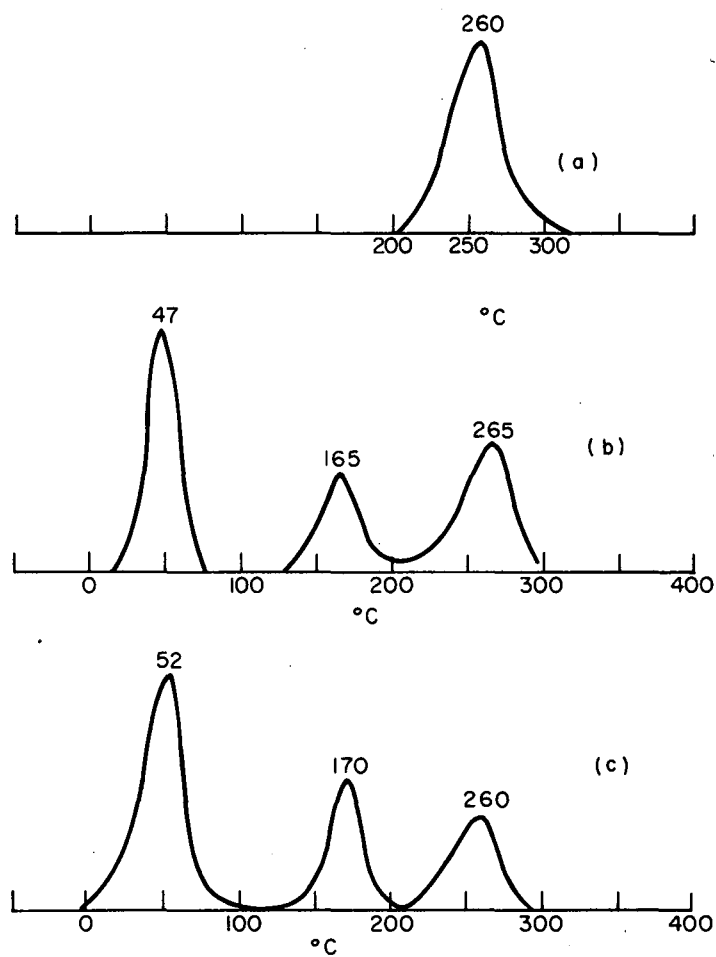
The results of the thermoluminescence studies on blue calcite are shown in Fig. 6. It was found that the naturally occurring blue calcite gave a single thermoluminescent glow peak at approximately 262°C. This peak apparently occurs at the same temperature at which the blue color is bleached by heating. When a sample of the calcite was irradiated with x rays for 30 minutes, two additional peaks appeared at temperatures of 52°C and 170°C.

Although the blue color could be obtained also by ultraviolet irradiation, there was no thermoluminescence in the calcite treated in this way.

An attempt was made to run glow curves on samples of precipitated calcite with various added impurity ions, such as Mn, Cu, Pb, and Fe, but no thermoluminescence was obtained from these samples, despite the fact that we were following the procedures developed by Medlin.²⁸

D. Discussion of Results

The thermoluminescence of calcite has been studied by several investigators. In a study by Lewis on dolomite and calcite, it was found that samples of calcite showed two thermoluminescent peaks before irradiation, at 240°C and at 310°C.²⁹ After x irradiation, a third peak of greater intensity than these two peaks occurred at 120°C. No correlation was made between these peaks and impurities present in the samples.



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Fig. 6. Glow curves on blue calcite:
(a) blue calcite (b) x-irradiated blue calcite
(c) x-irradiated bleached calcite.

A study by Parks showed that there were four peaks in natural calcite occurring at 75° , 125° , 205° , and 290°C . He found a direct correlation between the amount of alpha radioactivity and the intensity of the 290° peak in different calcite samples.³⁰

Only one attempt has been made to correlate the thermoluminescent peaks in calcite with specific impurities. Medlin carried out an investigation of the effects of impurity ions as activators in the thermoluminescence of precipitated calcite, and found a definite correlation between certain peaks and the concentrations of Pb and Mn in the samples. He found two peaks associated with Mn at 77° and 197°C , and two peaks associated with Pb at 27° and 137°C . Natural calcite showed no thermoluminescence, but upon x irradiation, gave two peaks, at 77° and 227°C .

The thermoluminescence experiments in this study were made to find out what differences existed between the blue calcite samples and the white calcite samples used by Medlin. The procedure followed was the same as used by Medlin.

From the widely varying results of the temperature at which glow peaks occur in different samples of calcite, it is presumed that the thermoluminescence of calcite or any mineral is dependent upon a number of factors, such as the presence of various impurity ions, lattice imperfections, and the geological history of the sample. For this reason, no attempt will be made to associate the two peaks at 52° and 170°C obtained from x-irradiated blue calcite with specific impurities present in the sample.

The thermoluminescent peak that is of greater interest is the one occurring at 262°C in unirradiated blue calcite, indicating a luminescent center of greater trap depth than the two additional ones obtained on x irradiating the sample. This peak occurs only in naturally blue calcite, or blue calcite which has been bleached and in which the blue color has been regenerated by the use of x rays. It also occurs at approximately the same temperature at which the blue color is bleached when the sample is heated. This glow peak is apparently associated with the same impurity as is responsible for the electron spin resonance.

That the blue color and the paramagnetic color centers can be produced by ultraviolet radiation, whereas no glow peak results from this type of irradiation, indicates that the energy of ultraviolet radiation is insufficient to produce a luminescent center, while it does rearrange electrons into traps which are associated with the color centers.

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APPENDIX

A. Spectrochemical Analysis

A spectrochemical analysis was made on the blue calcite and on several samples of white calcite for comparative purposes. Samples of from 3 to 5 mg were accurately weighed, dissolved in HCl, and diluted to 1 ml. Aliquots of 0.1 ml were taken for analysis and compared against a reagent blank. The analyses were made by George V Shalimoff of the Radiation Laboratory. The impurities detected by this method are reported below. (in μg per 500 μg of blue calcite).

Table II. Spectrochemical Analysis of blue calcite.

Impurity	<u>Al</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Na</u>	<u>Sr</u>	<u>K</u>	<u>Li</u>
Micrograms	0.08	0.1	0.05	0.5	0.01	1	<.05	<.01
Impurity	Be	Mn	As	Au	B	Co	Cr	
Micrograms	<.01	<.01	<.5	<1	<.05	<.05	<.01	

The analyses for K, Li, Be, Mn, As, Au, B, Co, and Cr were below the the limits of detectability of the analysis.

The results of the analysis of three different samples of white calcite are shown in Table III.

Table III. Spectrochemical analysis of samples of white calcite (μg per 500 μg of sample)

Impurities	<u>Li</u>	<u>Na</u>	<u>K</u>	<u>Be</u>	<u>Fe</u>	<u>Mn</u>
Sample a. Nye County, Nevada	<.01	0.05	0.1	<.01	0.01	0.1
Sample b. Crestmore, California	<.01	0.01	0.06	<.01	0.01	<.01
Sample c. Franklin, New Jersey	<.01	0.04	0.25	<.01	0.06	1

B. Quantitative Chemical Analyses

Since the electron spin resonance spectrum of the quartet in the blue calcite was of approximately the same intensity as the manganese lines, a quantitative analysis of manganese ion was made to determine the order of magnitude of the concentration of ion responsible for the color centers.

A standard manganese determination was used, in which the Mn^{++} was oxidized with sodium periodate to Mn^{+7} and compared with standard permanganate solutions.³¹ A 10-g sample of the blue calcite was dissolved in HNO_3 and 1 ml of concentrated phosphoric acid, and 0.2 g of sodium periodate was added. The solution was heated below boiling for 10 minutes and a deep purple color developed. The solution was diluted to 50 ml and compared against $2, 4, \text{ and } 8 \times 10^{-4} \text{ M}$ standard permanganate solutions in Beckman cells at a wave length of 575 m μ . By this method, the concentration of manganese was found to be 0.03 mole %.

To find the copper concentration, a standard method for determination of trace amounts of copper was used.³² The sample was dissolved in HNO_3 and perchloric acid, and HF was added to dissolve the residue. The method consists of the formation of a complex of the copper with diethyl dithiocarbamate, which is extracted into chloroform. The resulting yellow solution is compared against standard copper solutions in a Beckman absorption cell at 435 m μ . The concentration of copper by this method was found to be 0.003 mole %.

A semi-micro nephelometric procedure was used for the determination of halide ion concentration in blue calcite.³³ A 0.9-g sample of the calcite was dissolved in concentrated HNO_3 and diluted to a volume of 10 ml. Standards were made of NaCl solutions of 1, 3, 5, and $10 \times 10^{-5} \text{ M}$ concentrations. To each of these solutions was added 3 ml of approximately 1 % AgNO_3 solution. After the samples were heated for 20 minutes in a boiling water bath, the optical density of the

calcite solution was compared with the standards by using a Cary Spectrophotometer. The calcite solution was found to contain a concentration of 0.007 mole % halide ion.

C. Other Experiments

A determination of the radioactivity of the blue calcite and the rock which surrounds it as it is found in deposits was made by Bruce D. Wilkins, Lawrence Radiation Laboratory, Berkeley. The beta count on the calcite itself was found to be the same as the background count, while the surrounding material showed a small amount of radioactivity. This might be of sufficient magnitude to account for maintenance of blue color of the calcite by the effects of radiation from this surrounding rock.

An attempt was made to study the visible and ultraviolet spectrum of a blue calcite crystal and the effects of bleaching and x irradiation on the spectrum, but no significant results were obtained because of the high density of crystal fractures and imperfections in the blue calcite, making the sample nontransparent to ultraviolet and visible light.

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