Anisotropy of Color Centers in Calcite*

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In calcite colored by 3-Mev electrons (10^5 to 10^6 rads) at $-190°C$, two absorption bands at 350 and 290 $m\mu$ have been observed. Samples cut parallel to the c axis colored and measured with polarized light ($E_{\perp c}$ and $E_{\parallel c}$) showed that the band at 350 $m\mu$ is isotropic while that at 290 $m\mu$ is anisotropic. The former is correlated to trapped electrons and the latter to trapped holes. Both bands are stable at $-190°C$ but decay simultaneously at room temperature, accompanied by strong luminescence with a peak at 590 $m\mu$.

INTRODUCTION

COLOR-CENTER studies have for years concentrated on cubic crystals, particularly the alkali halides with NaCl structure,[1,2] and more recently the cesium halides[3,4] and alkaline earth fluorides.[5-8] Of the noncubic crystals, quartz (SiO_2),[9-11] corundum (Al_2O_3),[12] sodium nitrate ($NaNO_3$),[13] and a few others[14-16] have been investigated up to now. The color centers in quartz appear to be associated with aluminum impurities[11] since the intensity of coloration depends on the amount of Al present. The coloration of corundum, like that in very pure quartz, is very weak. In sodium nitrate the coloration is complicated by decomposition of the NO_3 complexes.[13]

Anisotropy of color centers in noncubic crystals has so far been established in quartz[9,11] and corundum.[17] In quartz for an electric vector perpendicular to the c axis ($E_{\perp c}$) the absorption peak is at 485 $m\mu$ and for $E_{\parallel c}$ at 460 $m\mu$. The difference is small and evidently not correlated to the crystal structure.

Past investigations in noncubic crystals have thus been largely complicated by impurities, resistance to coloration, or chemical instability. Calcite ($CaCO_3$) was selected in this study because large natural crystals of high purity and perfection were available and because calcite is known to be highly anisotropic.

EXPERIMENTAL PROCEDURE

Samples ($2\times2\times0.3$ cm) were cut parallel to the c axis from a large, clear crystal which showed no absorption between 0.21 and 1.0 μ. The direction of the c axis was located by means of a petrographic polarizing microscope. The cut samples were ground and polished with "Linde A" alumina powder.

For the coloration, electrons of 3 Mev (10^5 to 10^6 rads) produced by a Van de Graaff accelerator were used. Electrons have the advantage of providing large doses quickly, usually in less than one minute as compared to several hours for corresponding x-ray coloration.

To prevent bleaching, the coloration and subsequent absorption measurements were done in a cryostat at $-190°C$. The absorption measurements were made with a Beckman spectrophotometer, model DK-1, equipped with a calcite air-gap polarizer.

Figure 1 shows the absorption of a sample cut parallel to a cleavage plane, colored and measured with nonpolarized light, at $-190°C$. Coloration produces two absorption bands, at 350 $m\mu$ (3.54 ev) and at 290 $m\mu$ (4.28 ev), superimposed on the continuous increase of absorption toward higher energies. At room temperature the maxima remain in the same spectral position but the resolution is slightly less.
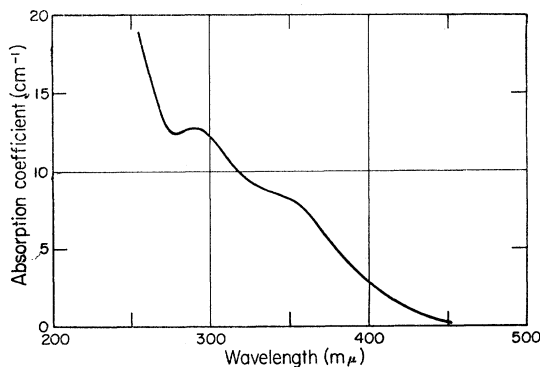
* Sponsored by the Navy Department under ONR contract.

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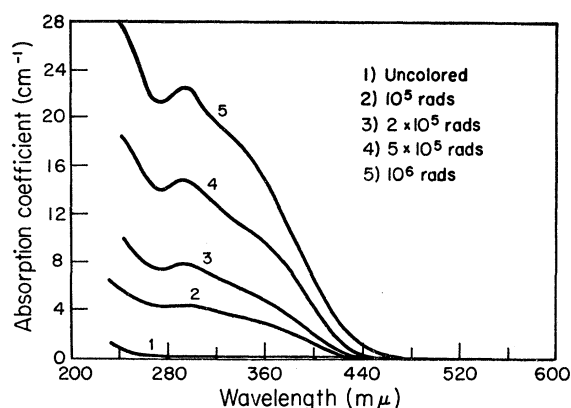[17] E. W. T. Mitchell, J. D. Rigden, and P. D. Townsend, Phil. Mag. **5**, 1013 (1960).

FIG. 1. Absorption of calcite (cut parallel to the cleavage plane) colored with 3-Mev electrons and measured at $-190°C$ with nonpolarized light.

FIG. 2. Absorption of calcite (cut parallel to c axis) colored with 3-Mev electrons and measured at $-190°C$ with polarized light $(E_{\perp c})$.

The absorption spectra of a sample cut parallel to the c axis and measured with polarized light for $E_{\perp c}$ and $E_{||c}$ are shown in Figs. 2 and 3. For $E_{\perp c}$ both bands are present while for $E_{||c}$ the 290-mμ band disappears but that at 350 mμ remains practically unchanged. Thus the latter is isotropic while that at 290 mμ is anisotropic.

The method for separating the two bands is shown in Fig. 4. The anisotropic band was obtained by subtracting the absorption for $E_{||c}$ from that for $E_{\perp c}$. To separate the isotropic band is was necessary to subtract the tail of the continuous absorption. This was some-
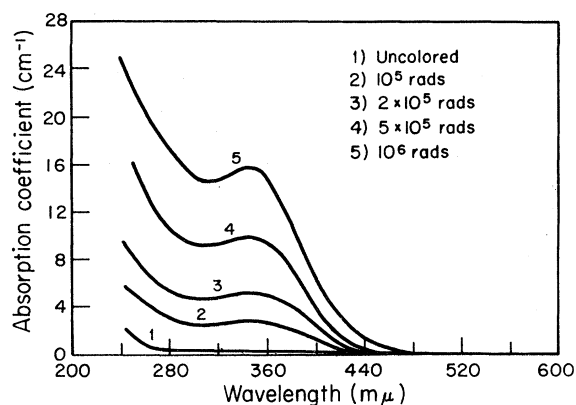

FIG. 3. Absorption of calcite (cut parallel to c axis) colored with 3-Mev electrons and measured at $-190°C$ with polarized light $(E_{||c})$.

what arbitrarily done in such a way that the band remained symmetrical. The half-width of both bands is approximately 0.8 ev and independent of coloration intensity.

The increase of the absorption maxima with the irradiation dose for both bands is shown in Fig. 5. The

coloration, fast in the beginning, later increases more slowly, similar to that of alkali halides. Whether a saturation exists could not be determined. The intensity ratio of both bands is independent of the degree of coloration.

At $-190°C$ both bands remain without any indication of bleaching for several hours. At room temperature, however, both bands decay simultaneously at about the same rate (Fig. 6). There is no simple exponential decay; the decay rate decreases with time.

Parallel with the thermal bleaching of the absorption bands, a strong orange luminescence takes place. The emission spectrum, measured with a Cary spectro-
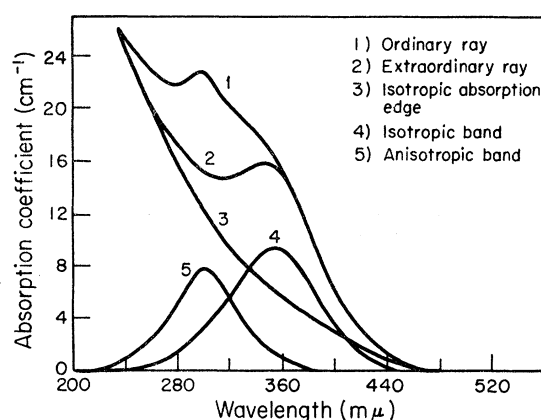

FIG. 4. Separation of isotropic and anisotropic bands.

photometer model 11, equipped with luminescence attachment, is shown in Fig. 7. The broad luminescence band has a peak at 590 mμ (2.10 ev), is isotropic, and shows no structure. Its decay seems to consist of at least two exponential processes (Fig. 8).

Absorption and emission have been measured simultaneously to determine whether there is a connection between the observed absorption bands and luminescence (Fig. 9). There is close agreement between the derivatives of the absorption maximum and the luminescence intensity. However, the luminescence at first decays more rapidly than the absorption.
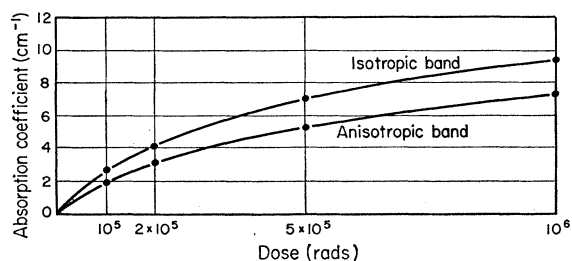

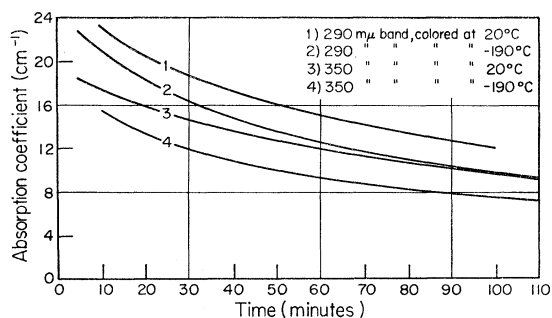FIG. 5. Increase of absorption maxima with coloration dose.

FIG. 6. Bleaching of absorption bands at room temperature.

DISCUSSION

The trigonal structure of calcite can be visualized as NaCl deformed along the body diagonal where Ca^{2+} ions take the place of Na^+, and CO_3^{2-} that of Cl^- ions. The oxygen atoms are arranged symmetrically around the C atoms in planes perpendicular to the c axis. (Fig. 10.) By electron bombardment internal ionization of all three atoms (Ca, C, O) may take place, but only the electrons with the weakest binding forces can remain outside their original state after irradiation. These are the valence electrons of the CO_3^{2-} complexes. In an ideal lattice, however, the trapping of these electrons is not possible; some defects (vacancies or impurities) must be present. Reduced to the simplest terms, the coloration consists of a transfer of electrons from CO_3^{2-}
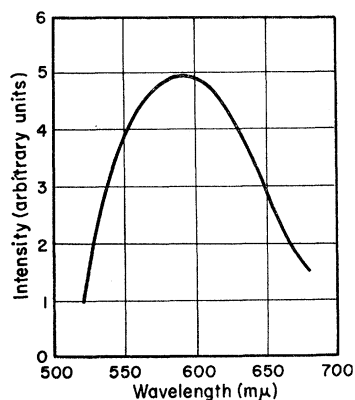
TABLE I. Efficiency of coloration.

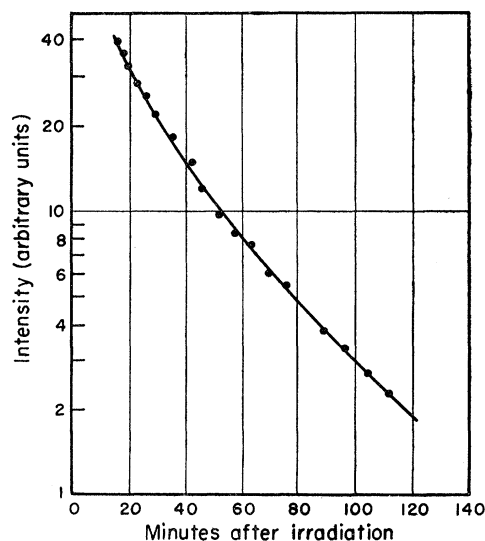| Radiation dose (rads)	Color centers per cm^3	Energy (ev)/center
5×10^4	6.9×10^{15}	3.2×10^2
2×10^5	1.2×10^{16}	7.1×10^3
1×10^6	3.2×10^{16}	1.4×10^4

FIG. 8. Change of emission with time.

band or to an intrinsic absorption edge modified by the presence of color centers.

Nothing is known concerning the presence of defects in uncolored calcite. According to Ievins and Straumanis,[18] colorless calcite samples may contain Sr, Mn, and Fe as impurities but not exceeding 0.0001%. These elements would form substitutional solid solutions and slightly distort the lattice only. The
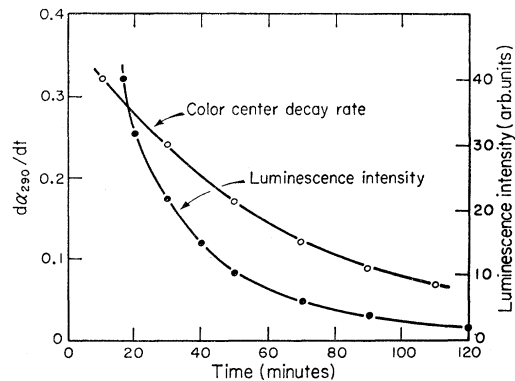

FIG. 7. Emission band of colored calcite at 20°C.

to Ca^{2+} ions, forming CO_3^- and Ca^+. In analogy to alkali halides Ca^+ can be considered a trapped electron (F center) and CO_3^- a trapped hole (V center).

The correlation of the two absorption bands results from the lattice structure of calcite. Since the position of Ca ions in the lattice is intrinsically isotropic, the 350-mμ band can be attributed to trapped electrons. The CO_3 complex, however, is anisotropic; the anisotropic band at 290mμ must therefore be correlated to a hole. The strong absorption increase at short wavelengths is isotropic. It can belong either to another

FIG. 9. Absorption and emission decrease with time.

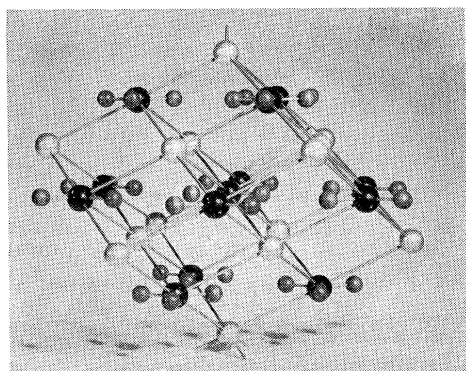[18] A. Ievins and M. Straumanis, Z. Physik 116, 194 (1940).

Fig. 10. Lattice structure of calcite.

concentration of color centers at highest coloration, computed by Smakula's formula,[19] is of the order

$10^{16}/cm^3$. If we assume that some defects may be created by irradiation, the defects originally present must be less than $10^{-6}/cm^3$. The efficiency of coloration is given in Table I.

At low coloration levels about 300 ev are required to form one color center. This is of the same order as in calcium fluoride.[20] The efficiency of coloration decreases rapidly with irradiation dose similar to other crystals.

The strong luminescence with an emission band at 590 mμ can be considered as the recombination of the trapped electron with the hole and simultaneous decrease of the absorption bands. This process (the reverse of coloration) depends on temperature. Illumination with light of a wavelength exceeding 280 mμ did not produce any noticeable effect on bleaching or luminescence, nor could a photocurrent ($>10^{-12}$ amp) be observed.

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Diagrammatic Expansion for the Ising Model with Arbitrary Spin and Range of Interaction*

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A new and simple diagrammatic expansion is developed for the free energy of the Ising model with arbitrary spin and range of interaction. The contribution of each diagram is a product of (1) the reciprocal of the order of the symmetry group of the diagram, (2) a product of semi-invariants, with a factor M_n for each spin in the diagram (n being the number of bonds joined to that spin) and (3) a sum of products $\Sigma_{i,j,k,\ldots}(2\beta J_{ij})(2\beta J_{kl})\cdots$, where $2\beta J_{ij}$ corresponds to a bond between spins i and j, and where the summation is carried out with no restrictions on the summation indices (i.e., no "excluded volume" corrections). The expansion variables are the spin deviation operators $\sigma_i \equiv \bar{S} - S_{iz}$. The quantity $\bar{S}$ is chosen to eliminate a large class of diagrams; this choice also minimizes the corresponding free-energy contribution and implies $\bar{S} = \langle S_{iz} \rangle$. By further renormalization of the vertices all reducible (i.e., simply articulated) diagrams are eliminated. To zero order the molecular field solution is obtained. The next approximation consists of the summation of renormalized simple loop diagrams. The justification of this choice of diagrams rests, at low temperature, on the decrease of the value of the higher order semi-invariants, on the relationship of these loop diagrams to the random phase approximation, and on the agreement with the rigorous low-temperature series result. At the Curie temperature the same choice of diagrams is justified by a modification of Brout's $1/z$ criterion, so that the expansion can be viewed as an expansion in $1/z$, where z is the effective number of spins interacting with a given spin. Finally the choice of loop diagrams is justified at high temperature by exact agreement to second order in T_c/T (and by a very close agreement to fourth order) with the rigorous high-temperature series expansion. Thus the theory agrees with rigorous results in the low-temperature and paramagnetic regions and has a well-defined criterion of validity in the intermediate temperature region. For nearest-neighbor interactions and spin $\frac{1}{2}$ the specific heat is continuous through the Curie temperature, with an infinite slope on the low-temperature side of the transition.

INTRODUCTION

THE Ising problem has been one of the most actively studied problems in statistical mechanics, principally due to its being perhaps the simplest model exhibiting a cooperative phenomenon, or phase transition.[1] In its simplest form, the spin-$\frac{1}{2}$ Ising model with

nearest-neighbor interactions, it serves as a useful model for several physical systems, such as the ordering of binary alloys. Of particular interest to us is the fact that the Ising Hamiltonian is part of the ferromagnetic Heisenberg Hamiltonian, and that the Ising problem is a convenient preliminary to the ferromagnetic problem;

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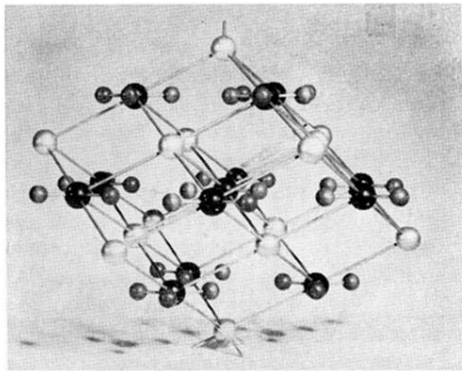
FIG. 10. Lattice structure of calcite.