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QUARTERLY REPORT NO. 5

ON

INFRARED STUDIES OF CRYSTALS II

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by

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I. PURPOSE OF THE RESEARCH

The general purpose of this research is to complete the investigations started in May of 1951 under Contract DA 36-039 sc-56736 on the infrared spectra and structure of barium titanate, brucite, mica, gypsum, and diamond.

II. ABSTRACT

During the period covered by this report the spectrum of brucite has been re-examined under higher resolving power at room temperature and at low temperature (liquid nitrogen). Several new features have been revealed. The spectrum of portlandite has also been re-examined under higher resolving power at room temperature and the similarity between this spectrum and that of brucite was confirmed, although the frequencies of the band maxima are slightly different. Preliminary observations have been made on the reflection spectrum of brucite in the region 10-14 microns.

The following laboratories in Europe were visited by Professor Sutherland during July and the early part of August:

- 1) Cavendish Laboratory - Cambridge
- 2) Clarendon Laboratory - Oxford
- 3) King's College Physics Laboratory - London
- 4) Centre National de Recherches Scientifiques - Bellevue, Paris
- 5) Sorbonne (Infrared Laboratory) - Paris
- 6) Chemistry Laboratories - Zurich
- 7) Physics Laboratory - Copenhagen

The study of the infrared dichroism of small crystals was continued and improvements made in the technique.

III. PUBLICATIONS

The work done during the period covered by this report has not yet been prepared for publication.

The work on gypsum was reported at the Ohio State Symposium in Molecular Spectra on June 15 in a paper entitled "The Infrared Spectrum of Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ " by M. Hass and G. B. B. M. Sutherland. The work on diamond was reported at a Diamond Conference held in Oxford, England, on July 1 in a paper entitled "Infrared Studies on Type I and Type II Diamonds" by G. B. B. M. Sutherland.

IV. FACTUAL DATAA. Barium Titanate

No further work to report.

B. Brucite

Crystal samples were prepared which are suitable for reflection spectra, one with the polished face perpendicular to the crystalline c-axis and one with the polished face parallel to the c-axis. This required a long process to obtain surfaces which were both flat and highly polished. In addition, time was spent on the construction of a reflection apparatus that can be fitted to Perkin-Elmer Models 12 and 112 spectrometers and can be flushed with dry nitrogen to reduce atmospheric absorption. Preliminary reflection spectra were obtained of the 1μ to 15μ region, special emphasis being placed on the region beyond 10μ , where brucite begins to absorb very strongly. Present indications are that the position of the strong band beyond 12μ can be located in this way.

Our Perkin-Elmer Model 21 double-beam spectrometer has recently been equipped with a CaF_2 prism. This was used to examine a thin crystal of brucite with its faces parallel to the c-axis of the crystal. After much labor, we succeeded in obtaining a crystal about 100μ thick. The thinnest specimen obtained previously was about 250μ thick (see Technical Report No. 2). This thin crystal enabled us to see for the first time some of the details in the region about 2.7μ when the c-axis of the crystal is parallel to the electric vector in the incident radiation. In the past, the region from 2.6μ to 2.8μ was completely absorbing.

The CaF_2 prism resolved all the peaks that had previously been resolved by the LiF prism (see Technical Report No. 2). In addition, it now

appears that the strong absorption which appears near 2.73μ only when there is a component of the electric vector parallel to the c-axis, may be composed of three or four bands, all having the same dichroic properties. The present evidence for this is fairly conclusive, but additional checks are planned for the future.

The low temperature (i.e., liquid nitrogen) spectra were also repeated using the higher resolving power. For a specimen in which the c-axis is perpendicular to the electric vector of the incident radiation, the 2.73μ band appears weakly at room temperature. Near liquid air temperature, this band has disappeared completely. In addition, the bands at 2.83μ and 3.07μ are missing entirely at this temperature. When the c-axis is parallel to the electric vector, it is difficult to say to what degree the absorption near 2.73μ is decreased by the reduction in temperature. However, there seems little doubt that there is a reduction in intensity at that position. For this orientation the bands near 2.83μ and 3.07μ are also missing at the low temperature. This result leaves little doubt that these two absorptions are difference bands. In addition, it was noted that most of the other bands in the region from 2μ to 3.1μ were reduced somewhat in intensity at low temperatures. Those which showed a decrease in intensity also shifted slightly to higher frequencies at low temperatures.

A spectrum of a single crystal of $\text{Ca}(\text{OH})_2$ (portlandite) was obtained using a CaF_2 prism with the c-axis perpendicular to the incident electric vector. This was qualitatively the same as the brucite spectrum even in the details given by this higher resolving power.

Current modifications being made on the multi-pass grating spectrometer prevented the re-examination of the 2.7μ region of the brucite spectrum at the very high resolving power afforded by that instrument.

C. Micas

No further work to report.

D. Gypsum

No further work to report.

E. Infrared Dichroism of Single Crystals in Converging Light

An ancillary piece of equipment has been constructed for the measurement of reflection spectra on a Perkin-Elmer 12B spectrometer. It has been made gas tight so that dry nitrogen can flow through it and eliminate atmospheric bands which are troublesome in making accurate intensity measurements.

Some measurements of dichroism have been made by reflection from materials which have bands with low dichroism as measured by absorption in order to check the work mentioned in the last quarterly report (No. 4).

V. CONCLUSIONS

A. Barium Titanate

Nothing to report.

B. Brucite

It now appears certain that many of the anomalous bands found in brucite are due to combination of the OH stretching fundamental with low frequencies probably due to other motions of the hydrogen atoms.

C. Micas

Nothing to report.

D. Gypsum

Nothing to report.

E. Infrared Dichroism of Single Crystals and Converging Light

No definite conclusions are possible until further experiments have been made.

VI. FUTURE PROGRAM

A. Barium Titanate

If time permits, some work will be done on large single crystals of barium titanate.

B. Brucite

A theoretical study will be made of the anomalies in the brucite spectrum.

C. Micas

High resolution work will be done if time permits. Results will be

prepared for publication.

D. Gypsum

Results will be prepared for publication.

E. Infrared Dichroism of Single Crystals and Converging Light

Work will continue along lines indicated in previous reports.

F. Diamonds

Results will be prepared for publication.

VII. PERSONNEL

The following have been engaged on the work reported here:

Professor G. B. B. M. ~~Sutherland~~ Sutherland, Director (part time)

Dr. R. T. Mara (full time)

Mr. A. Dockrill (technician 1/3 time)

Mr. R. Hede (graduate student 1/4 time)

